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An *ab initio* study of $\text{Fe}(\text{CO})_n$, $n=1,5$, and $\text{Cr}(\text{CO})_6$

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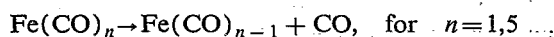
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Ab initio calculations have been performed for $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_n$, $n=1,5$. Basis sets of better than double zeta quality are used and correlation is included using the modified coupled-pair functional method. The computed geometries and force constants are in reasonable agreement with experiment. The sequential bond dissociation energies of CO from $\text{Fe}(\text{CO})_5$ are estimated to be: 39, 31, 25, 22, and >5 kcal/mol. We note that the first bond dissociation energy is relative to the singlet ground state of $\text{Fe}(\text{CO})_5$ and the lowest singlet state of $\text{Fe}(\text{CO})_4$, whereas the second is relative to the ground triplet states of $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$. In addition, the binding energy for Fe-CO would be modified to 18 kcal/mol if dissociation occurred to the $\text{Fe}(^5F)$ excited state asymptote. The CO binding energies for Fe and Cr are found to be in poorer agreement with experiment than those found in a previous study on $\text{Ni}(\text{CO})_4$. The origins of this difference are discussed.

I. INTRODUCTION

There is a great deal of interest in understanding the bonding in organometallic compounds, which are often important in heterogeneous catalysis (see Ref. 1, for example). The average metal-ligand binding energies for many saturated organometallics have been known for some time (Refs. 1-3 and references therein, for example). However, a critical factor in the chemistry of these systems is not the average bond energy, but rather the energy required to remove individual ligands, perhaps in a particular sequence.³ While such data may be available, the experiments can be quite difficult to perform and/or interpret; in some cases it requires two experiments, potentially of very different accuracy, to determine the value of interest (see below). *Ab initio* calculations can provide a valuable alternative source of such binding energies. In addition the calculations provide insight into bonding mechanisms which is not readily obtained from experimental data.

An example of the importance of individual fragment binding energies is the photodissociation of $\text{Fe}(\text{CO})_5$. The series of photodissociation processes

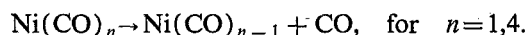


have been extensively studied experimentally (see Refs. 4-7, for example). The photodissociation dynamics can be accurately modeled by various statistical methods, given accurate binding energies of the individual $\text{Fe}(\text{CO})_n$ fragments.⁷ There has been only one determination of all the binding energies for the $\text{Fe}(\text{CO})_n$ fragments,⁸ and there is a large experimental uncertainty for several of these, as well as disagreement with a more recent determination of the first CO dissociation energy from $\text{Fe}(\text{CO})_5$.⁹ Adjustment of these binding energies by up to 10 kcal/mol can bring most of the statistical models into agreement with

experimental data, so errors in the experimental binding energies are the main source of difficulty in the modeling process.⁷

The self-consistent-field (SCF) level of theory has been successfully used to gain insight into the nature of the bonding in $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ by decomposing the bonding into various components.¹⁰ In $\text{Fe}(\text{CO})_5$ the difference in the nature of the bonding between the axial and equatorial carbonyls was clearly demonstrated using this decomposition of the SCF wave function. Furthermore, the difference between the bonding in $\text{Ni}(\text{CO})_4$, where the $3d$ shell is filled, and $\text{Fe}(\text{CO})_5$ with an empty $3d_{z^2}$ orbital was also visible. However, while low levels of theory have given valuable qualitative insight into these systems, in general, only the highest levels of theory can be used for a quantitative study. For example, the SCF model fails to yield reasonable metal-ligand bond lengths for $\text{Fe}(\text{CO})_5$ (Refs. 11 and 12) or $\text{Fe}(\text{C}_5\text{H}_5)_2$.^{13,14} $\text{Fe}(\text{CO})_5$ is an interesting case in that the SCF model yields a reasonable bond length and force constant for the equatorial CO ligands but very poor results for the axial CO ligands. The inclusion of correlation using a multireference configuration interaction (CI) approach has been shown to correct the deficiencies of the SCF model and results in bond lengths and force constants for $\text{Fe}(\text{CO})_5$ which are in good agreement with experiment.¹² The inclusion of correlation also leads to an Fe-C₅H₅ distance in ferrocene ($\text{Fe}(\text{C}_5\text{H}_5)_2$) that is in good agreement with experiment.¹⁵

In addition to accurate geometries and force constants, knowledge of the ligand binding energies is very important, as noted above. While multireference CI approaches have been successful in obtaining improved bond lengths and force constants, they have had much less success for the ligand binding energies, especially for a series of binding energies for processes such as¹⁶



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The problem arises because all the metal valence ($3d$ and $4s$) and ligand valence ($3 - 5\sigma$ and 1π) electrons must be correlated to obtain an accurate binding energy. Thus, the CI expansion becomes very long for even the smallest systems. The introduction of additional approximations inevitably leads to poor results, or at least results of differing accuracy for each n .

One way of avoiding such problems is to use a size-extensive single-reference-based approach. If a sufficiently high percentage of the correlation energy is obtained for all systems, one expects equally reliable results for similar systems containing different numbers of ligands. Recently the modified coupled-pair functional (MCPF) method was applied to the CO binding energies for the $\text{Ni}(\text{CO})_n$ series.¹⁶ The net CO binding energy of 120 kcal/mol for $\text{Ni}(\text{CO})_4$ was in quite good agreement with the thermochemical value of 140 kcal/mol.¹⁷ However, the individual CO binding energies of 30, 29, 36, and 24 kcal/mol (for $n = 1, 2, 3$, and 4) differ significantly from the experimental values of 29 ± 15 , 54 ± 15 , 13 ± 10 , and 25 ± 2 kcal/mol.¹⁸ Since the overall binding energy in the MCPF treatment is reasonable, and the calculations were expected to have approximately equal accuracy for all the systems, it was concluded that the experimental determination of the individual binding energies was probably in error. The experimental binding energies for the individual CO ligands were derived from a combination of two experiments, the photoelectron spectroscopy measurements of Stevens *et al.*¹⁸ and the negative ion appearance potential measurements of Compton and Stockdale.¹⁹ As the photoelectron spectroscopy measurements are expected to be quite accurate, it appeared that the appearance potential measurements must be in error. Recently, this has been confirmed²⁰ and now there is general agreement between theory and experiment for the $\text{Ni}(\text{CO})_n$ binding energies.

Given the success of the MCPF method for computing the Ni-CO binding energies of the $\text{Ni}(\text{CO})_n$ series, and the uncertainty of the experimental $\text{Fe}(\text{CO})_n$ binding energies, we have investigated the $\text{Fe}(\text{CO})_n$ series of molecules using the MCPF method. We have also investigated the total $\text{Cr}-(\text{CO})_6$ binding energy of $\text{Cr}(\text{CO})_6$ to determine whether this method can be generally applied to organometallic systems, or at least saturated organometallics. We find that the MCPF method gives only qualitative results for the binding energies of both the $\text{Fe}(\text{CO})_n$ series and $\text{Cr}(\text{CO})_6$, although the geometries and force constants of $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ are in reasonable agreement with experiment. For both $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ the MCPF calculations yield a smaller percentage of the total metal-CO binding energy than calculated for $\text{Ni}(\text{CO})_4$, and the individual binding energies for the $\text{Fe}(\text{CO})_n$ ($n = 1, 4$) fragments are not as well determined. We discuss reasons for the difference in accuracy between the current systems and the Ni system later.

In Sec. II we discuss details of the methods used, and in Sec. III we present our results and discussion, first presenting the results for $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$, and then the $\text{Fe}(\text{CO})_n$ fragments. In Sec. IV we present our conclusions.

II. METHODS

For Fe and Cr we use the ($14s\ 9p\ 5d$) primitive Gaussian basis set of Wachters,²¹ contracted using his number 2 scheme to [$8s\ 4p\ 3d$]. Two diffuse p functions, as recommended by Wachters, and the diffuse d function of Hay²² are added, yielding final basis sets of the form ($14s\ 11p\ 6d$)/[$8s\ 6p\ 4d$]. The C and O basis sets are [$4s\ 3p$] contractions of the ($9s\ 5p$) primitive Gaussian set of van Duijneveldt.²³ The s and p spaces are contracted (5211) and (311), respectively. In all calculations, only the pure spherical harmonics are used. Previous work on the $\text{Ni}(\text{CO})_n$ series^{16,24} has explored the effect of larger Ni and CO basis sets on the CO binding energies; the current basis sets are expected to yield binding energies accurate to about 2–3 kcal/mol per CO.

The orbitals are optimized in an SCF calculation including symmetry and equivalence restrictions. As discussed above, for the $\text{Ni}(\text{CO})_n$ series it is necessary to correlate all of the Ni and CO valence electrons to determine an accurate D_e . Thus we correlate the metal $3d$ and $4s$ electrons and the ten valence electrons on each CO, giving for example 58 electrons to be correlated for the $\text{Fe}(\text{CO})_5$ molecule. As noted previously, when this many electrons are correlated, a size-extensive method is essential, and we use the MCPF method.²⁵ For open-shell systems we impose the first-order interacting space restriction²⁶ to reduce the CI expansion length. This is not expected to affect the accuracy of the computed properties. The most important relativistic effects (the Darwin and mass-velocity terms) are included in certain cases using first-order perturbation theory.^{27,28}

In general, we optimize both the metal-C and C-O bond lengths. The metal-C stretch has a broad potential and the computed force constant is rather stable to the specific points used in the fitting procedure. However, the C-O stretching potential is much tighter and therefore the force constant is sensitive to the points used, even though the bond length is not. As the calculations for the larger systems are computationally intensive, we do not always have a grid of points suitable for the calculation of the C-O force constant, thus we only report the M-C force constant. Since we used only symmetric displacements of the M-C and C-O bond distances, we obtain symmetry force constants. These are dominated by the internal force constant F_{MC} but also contain contributions from the coupling of the different M-C stretches, or the internal force constants $F_{\text{MC},\text{M}'\text{C}}$.

The calculations were performed on the NASA Ames CRAY X-MP/48 and NAS CRAY Y-MP/832 computers using the MOLECULE-SWEDEN²⁹ program system.

III. RESULTS AND DISCUSSION

A. Saturated carbonyls

In Table I we present a summary of some previous work on $\text{Ni}(\text{CO})_4$ (Ref. 24) and also include force constant information which was not presented previously. This work was carried out in a basis equivalent to that used here, also using the MCPF approach. Overall, there is

TABLE I. Summary of the $\text{Ni}(\text{CO})_4$ results from previous work. The bond lengths r are in a_0 , the total CO binding energy BE is in kcal/mol, and the force constant k is in mdyne/ \AA .

	$r(\text{Ni-C})$	$r(\text{C-O})^a$	BE	$k(\text{Ni-C})$
MCPF ^b	3.558	2.206	117.5	2.13
Experiment	3.473 ^c	2.156 ^c	140(144) ^d	2.36(2.10) ^c

^aFor comparison, the free CO bond length at this level of treatment is $2.185 a_0$ compared to the experimental value of $2.132 a_0$.

^bBond distances and binding energy taken from Bauschlicher *et al.* (Ref. 24). Note that there is an error in the bond lengths given in Table 3 of this paper for $\text{Ni}(\text{CO})_4$. See also Blomberg *et al.* (Ref. 16) for similar results at the MCPF level in a different basis set. They obtain a binding energy of 120 kcal/mol. The force constant is derived from the results of Bauschlicher *et al.* (Ref. 24).

^cThe bond distances and force constants are from Hedberg *et al.* (Ref. 53). The force constant is for the symmetric stretch, F_{22} in the notation of Hedberg *et al.* The value in parentheses corresponds to the internal force constant F_{MC} .

^dThe experimental binding energy corresponds to D_0^{298} , taken from Fischer *et al.* (Ref. 17). The value in parentheses corresponds to D_e derived using the results of Ross *et al.* (Ref. 54) and Jones *et al.* (Ref. 55).

good agreement between theory and experiment. The MCPF method recovers 82% of the experimental binding energy. The Ni-C distance is somewhat too long, due to the low binding energy, although the agreement is still quite good. The C-O bond distance is also too long, but since improving the CO basis set yields a free CO bond length in good agreement with experiment,³⁰ it is likely that much of the error in the CO bond distance in $\text{Ni}(\text{CO})_4$ arises from limitations in the basis set. However, as discussed previously, this is not expected to affect other computed properties, such as the binding energy. A similar situation occurs for $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$ (see below). The Ni-C force constant is also in reasonable agreement with experiment, being somewhat too small, in accord with the low binding energy and long Ni-C bond distance.

We now consider the saturated systems $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$. Both of these molecules are known to be closed-shell systems with high symmetry, O_h and D_{3h} , respectively. We optimize both the metal-C and C-O bond distances with these symmetry constraints. Our results, along with previous calculations and experiment, are summarized in Tables II and III.

We first discuss the $\text{Cr}(\text{CO})_6$ results from Table II. The C-O bond distance in $\text{Cr}(\text{CO})_6$ is too long, as found for $\text{Ni}(\text{CO})_4$. The error in the Cr-CO bond length in $\text{Cr}(\text{CO})_6$ is similar to the error in the Ni-CO bond length in $\text{Ni}(\text{CO})_4$ at the same level of theory. However, the total CO binding energy for $\text{Cr}(\text{CO})_6$ is only 68% of the experimental D_e value, in marked contrast to $\text{Ni}(\text{CO})_4$ where the MCPF method yields 82% of the experimental binding energy. It is interesting to note that the error in the metal-C bond length is similar for $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$ despite the difference in the accuracy of the binding energies, and that the agreement between the experimental and theoretical force constants is also quite good in each case. This suggests that our description in the equilibrium region is good for both $\text{Cr}(\text{CO})_6$ and $\text{Ni}(\text{CO})_4$, but we are not describing the molecule and separated sys-

TABLE II. Summary of the $\text{Cr}(\text{CO})_6$ results. The bond lengths r are in a_0 , the total CO binding energy BE is in kcal/mol, and the force constant k is in mdyne/ \AA .

	$r(\text{Cr-C})$	$r(\text{C-O})$	BE	$k(\text{Cr-C})$
MCPF	3.696	2.216	109.5	2.06
Previous work				
$X\alpha^a$	3.531	2.160	207.0	3.19
DFT ^b	3.616	...	153	2.2
SDCI ^c	3.616	2.154	200	
Experiment	3.616 ^d	2.154 ^d	154(162) ^e	2.44(2.08) ^f

^aBaerends *et al.* (Ref. 31), LCAO- $X\alpha$ method, extended basis set.

^bZiegler *et al.* (Ref. 32), density functional theory. Calculations carried out at experimental Cr-C bond distance, free C-O bond distance. Force constant calculated with different functional than binding energy.

^cMoncrieff *et al.* (Ref. 33), SDCI using experimental geometry.

^dThe bond distances are from Jost *et al.* (Ref. 56). See also Rees *et al.* (Ref. 57).

^eThe experimental binding energy corresponds to D_0^{298} , taken from Pittam *et al.* (Ref. 58). The value in parentheses corresponds to D_e derived using the data summarized by Pilcher *et al.* (Ref. 59).

^fThe force constants are from Jones *et al.* (Ref. 60). The force constant is for the symmetric stretch, F_{22} in the notation of Jones *et al.* The value in parentheses corresponds to the internal force constant F_{MC} .

tems as well for $\text{Cr}(\text{CO})_6$ —we discuss this point in more detail after analyzing the $\text{Fe}(\text{CO})_5$ results.

The results of Baerends *et al.*³¹ using the $X\alpha$ approach are also summarized in Table II. The $X\alpha$ method yields a binding energy which is significantly larger than the experimental value, resulting in a Cr-C bond distance which is too short and a force constant which is too large. The density functional approach used by Ziegler *et al.*³² yields a Cr-CO binding energy and force constant which are both in good agreement with the experimental values. We note that Ziegler *et al.* used the experimental Cr-C and free C-O bond distance for $\text{Cr}(\text{CO})_6$. This will probably not affect the computed binding energy or force constant significantly, however. The singles and doubles CI (SDCI) results of Moncrieff *et al.*³³ for $\text{Cr}(\text{CO})_6$, given in Table II, are overbound by about the same amount as the $X\alpha$ results. This is probably due to basis set superposition errors in this case, since Moncrieff *et al.* used a basis set which is single ζ in the core region. This can lead to large superposition errors when six carbonyls are coordinated to the chromium atom.

The $\text{Fe}(\text{CO})_5$ results are summarized in Table III. All of the bond lengths are too long at the MCPF level as expected from the $\text{Ni}(\text{CO})_4$ and $\text{Cr}(\text{CO})_6$ results. However, the error in the axial and equatorial Fe-C bond lengths is not the same. The equatorial Fe-C distance has an error of $0.04 a_0$, while the axial distance has about three times the error, $0.13 a_0$, when compared with the electron diffraction results for $\text{Fe}(\text{CO})_5$.³⁴ The MCPF results are a great improvement over the SCF values, where the errors are 0.09 and $0.45 a_0$, respectively. In addition to improving the Fe-C bond lengths, the MCPF method yields a dramatic improvement in the force constants. As has been discussed previously,^{10,12} the bonding between the Fe atom and the axial and equatorial CO ligands is very different. The Fe atom in $\text{Fe}(\text{CO})_5$ is best viewed as having a $3d^8$

TABLE III. Summary of the $\text{Fe}(\text{CO})_5$ results. The bond lengths r are in \AA , the total CO binding energy BE is in kcal/mol, the force constants k are in mdyne/\AA , and the ionization potential IP is in eV.

	Axial			Equatorial		
	$r(\text{Fe-C})$	$r(\text{C-O})$	$k(\text{Fe-C})$	$r(\text{Fe-C})$	$r(\text{C-O})$	$k(\text{Fe-C})$
MCPF	3.548	2.208	2.78	3.490	2.224	2.91
Previous work						
SCF ^a	3.868	...	0.5	3.541	...	1.5
CI(10B) ^a	3.398	...	3.3	3.467	...	2.8
$X\alpha$ ^b	3.353	...	4.04	3.398	...	2.78
DFT ^c	3.344	3.383
Experiment	3.414 ^d	2.177 ^d	3.02(2.57) ^e	3.453 ^d	2.177 ^d	3.20(2.64) ^e
	IP	BE				
MCPF	7.75 ^f	94.2(97.1) ^g				
Previous work						
$X\alpha$ ^b		231.5				
DFT ^c		141.4				
Experiment	7.877 ^h	142(141) ⁱ				

^aLüthi *et al.* (Ref. 12), SCF and contracted CI calculation CI(10B).^bRösch *et al.* (Ref. 37), LCGTO- $X\alpha$ method.^cZiegler *et al.* (Ref. 32), density functional theory.^dBond distances from Beagley and Schmidling (Ref. 34).^eThe force constants are from Jones *et al.* (Ref. 35). The force constant is for the symmetric stretch, F_{33} for the equatorial force constant, and F_{44} for the axial force constant, in the notation of Jones *et al.* The value in parentheses corresponds to the internal force constant F_{MC} .^fThe vertical IP. The MCPF IP for Fe atom is 7.49 eV, compared to the experimental value of 7.87 eV (Ref. 61).^gValue in parentheses includes the relativistic correction at the nonrelativistic geometry.^hNorwood *et al.* (Ref. 43).ⁱThe experimental binding energy corresponds to D_0^{298} , after Behrens (Ref. 62). The value in parentheses corresponds to D_e derived from the results of Behrens. In a recent photoelectron-photoion coincidence study of $\text{Fe}(\text{CO})_5$, Norwood *et al.* (Ref. 43) obtain $\Delta H_{f,298}^0(\text{Fe}(\text{CO})_5(\text{g})) = -179.2 \pm 1.7$ kcal/mol, giving a binding energy (D_e) of 147.4 kcal/mol.

occupation with an empty $3d_{z^2}$ orbital. Therefore, 5σ donation is much more important for the axial ligands than the equatorial ligands. It appears that the SCF model is not able to correctly describe the 5σ donation as well as the $3d$ to CO $2\pi^*$ donation. The MCPF method is able to describe both types of bonding more reliably, leading to better bond lengths and force constants. Unfortunately, there still appears to be some bias in the results, since the error in the axial Fe-C distance is larger than for the equatorial Fe-C distance. In fact, the error is sufficiently large that the MCPF method predicts the axial distance to be longer than the equatorial distance, in contrast to the electron diffraction results shown in Table III. It is interesting to note, however, that our results are in agreement with the comments of Jones *et al.*,³⁵ that based on vibrational spectra and force constants of $\text{Fe}(\text{CO})_5$, one would expect the Fe-C equatorial bond length to be shorter than the axial. In addition, the refinement model used to interpret the electron diffraction results³⁴ constrained the axial and equatorial C-O bond distances to be equal and refined the Fe-C bond distances, whereas we find the C-O bond distances to be different. It would be interesting to know the result of a refinement with the Fe-C distances constrained to be equal and the C-O distances allowed to be different, which should be possible with the same experimental data. Of course, an experiment which yields both axial and equatorial Fe-C and C-O bond distances would be the ideal solution. In relation to this, Shriver and Whitmire³⁶ note

that x-ray diffraction results indicate that the axial and equatorial Fe-C bond lengths are equal to within ± 0.006 a.u. in crystalline $\text{Fe}(\text{CO})_5$. However, it is still probable that the axial Fe-C bond distance is too long at the MCPF level.

The ionization potential of $\text{Fe}(\text{CO})_5$ computed using the MCPF method is in error by 0.13 eV, which is smaller than for Fe atom, where the error is 0.38 eV. Part of this reduction in error for $\text{Fe}(\text{CO})_5$ is probably due to the fact that the electron is not removed completely from the Fe, but rather part from the Fe and part from the CO.

The results of the CI(10B) treatment of $\text{Fe}(\text{CO})_5$ by Lüthi *et al.*¹² are summarized in Table III. This calculation predicts that the axial Fe-C bond distance is shorter than the equatorial value, in agreement with the electron diffraction results. However, the difference is too large: the error in the equatorial distance is $+0.017$ a.u., while the axial distance is in error by -0.017 a.u. Thus it appears that the CI(10B) treatment is biased in favor of the axial Fe-C bond. The fact that the axial Fe-C force constant is larger than the experimental value whereas the equatorial force constant is smaller than the experimental value supports this. However, the difference between the experimental and theoretical bond lengths is less for the CI(10B) treatment than for the MCPF method.

The $X\alpha$ results of Rösch *et al.*³⁷ for $\text{Fe}(\text{CO})_5$ suffer from the same overbinding as found for $\text{Cr}(\text{CO})_6$, with this method yielding 165% of the experimental binding.

Thus it is not surprising that the Fe–C bond lengths are too short. In contrast to the SCF results, where the axial force constant is much too small, the $X\alpha$ method gives an axial force constant which is much too large. Based on the errors in the bond lengths and force constants, it appears that the $X\alpha$ method, unlike the SCF, has a larger error for the axial groups, having them over bound by more than the equatorial groups.

The net CO binding energy for $\text{Fe}(\text{CO})_5$ obtained with the MCPF method is only 67% of the experimental D_e value. Inclusion of the relativistic correction increases the binding energy by only 3 kcal/mol, so this is not a large effect. The value of 67% for $\text{Fe}(\text{CO})_5$ is very similar to the 68% found for $\text{Cr}(\text{CO})_6$, but is significantly smaller than the 82% found for $\text{Ni}(\text{CO})_4$. Since the error in the bond lengths is similar for all three systems and the force constants are in reasonable agreement with experiment, it might seem surprising that the MCPF method is recovering a smaller percentage of the binding energy for $\text{Cr}(\text{CO})_6$ and $\text{Fe}(\text{CO})_5$ than $\text{Ni}(\text{CO})_4$. However, there are some differences between $\text{Ni}(\text{CO})_4$ and the other two systems. All of the molecules have singlet ground states, and SCF calculations¹⁰ for $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$, and $X\alpha$ calculations for $\text{Cr}(\text{CO})_6$ (Ref. 31) have shown that the overlap of the 4s orbital with the CO ligand is very unfavorable energetically. Therefore the metal promotes the 4s electron into the 3d shell and the bonding is derived from the metal $3d^{n+2}$ asymptote; this is $t_2^6 e^4$ for Ni, $e^4 e'^4$ for Fe, and $t_2^6 g$ for Cr. This simple picture is naturally modified by the large metal to CO $2\pi^*$ backdonation, and for $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ by the ligand to metal σ donation. However, it is clear that the metal atoms in the compound are associated with excited atomic asymptotes. For Ni the $3d^{10}$ asymptote is 1.7 eV above the ground state. For Fe and Cr the singlet states arising from $3d^{n+2}$ have not been observed, but even the lowest state from this occupation is 4.1 eV above the ground state for Fe and 4.4 eV for Cr. Thus a much greater promotion energy is required for Fe and Cr than for Ni. It is well known that it is difficult to correctly position transition metal atomic states with different numbers of 3d electrons (see below), with the calculations having a strong bias in favor of those states with fewer 3d electrons.³⁸ In addition to the promotion energy, the high-spin coupling exchange energy of the Fe and Cr atomic ground states is lost in the molecule. The promotion energy and loss of exchange energy must be counterbalanced by the metal–CO bond energy, which is usually underestimated by *ab initio* methods. As exchange energy is usually computed reasonably accurately at low levels of theory, the underestimation of the strength of the metal–CO bond (even relative to the metal $3d^{n+2}$ asymptote) and overestimation of the promotion energy leads to too small a net binding energy. As the promotion energy and loss of exchange energy are larger for Cr and Fe the calculations obtain a smaller percent of the binding energy.

This argument is supported by accurate calculations³⁹ on Be_4 . As in the case of the metal carbonyls, the free metal atom is very different from that in the compound; the ground state of Be is $1S(2s^2)$ whereas in the cluster it is

strongly *sp* hybridized. However, Be_4 is a sufficiently simple system that very high levels of theory can be used to compute an accurate binding energy. These Be_4 calculations show that the bond lengths and vibrational frequencies converge much more rapidly than the binding energy, since the Be atom hybridization is not changing near equilibrium. A similar situation is occurring for the transition metal carbonyls.

Ziegler *et al.*³² obtain very good results for the binding energy and bond distances of $\text{Fe}(\text{CO})_5$ using the density functional method. We note that they did not present any force constant information for $\text{Fe}(\text{CO})_5$, although they did so for $\text{Cr}(\text{CO})_6$, and they also constrained the C–O bond distance to that of free CO. However, this constraint will probably not affect the computed binding energy significantly. Ziegler *et al.* give the $3d^8$ excited state to $3d^6 4s^2$ Fe ground state separation as 118 kcal/mol computed using density functional theory. A similar calculation with the MCPF method yields a separation of 162 kcal/mol, or 44 kcal/mol larger (as noted above, this separation is not known experimentally). This 44 kcal/mol is very close to the 45 kcal/mol difference in the binding energy of $\text{Fe}(\text{CO})_5$ from the two methods, supporting our contention that errors in the description of the atomic asymptotes lead to errors in the binding energy for $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ using the MCPF method. In this regard, we note that for $\text{Ni}(\text{CO})_4$, the error in the atomic Ni $3d^{10}(^1S)$ to $3d^9 4s(^3D)$ ground state separation computed using the MCPF approach is 11 kcal/mol. This leads to an increase in the binding energy of $\text{Ni}(\text{CO})_4$ if we dissociate to the singlet asymptote and then use the experimental separation to obtain ground state Ni and CO. Thus the overall binding energy (128.5 kcal/mol) is increased to 89% of the experimental result.

B. $\text{Fe}(\text{CO})_n$, $n=1,4$

In this section we consider successively removing CO molecules from $\text{Fe}(\text{CO})_5$. The overall energetics are summarized in Fig. 1. Our results for $\text{Fe}(\text{CO})_4$ are shown in Table IV. $\text{Fe}(\text{CO})_4$ is known to have a triplet ground state⁴⁰ and C_{2v} symmetry.⁴¹ The geometry is a distorted tetrahedron where the angle between one pair of CO ligands increased and the other decreased, so there are two equivalent pairs of CO ligands. An alternative description of $\text{Fe}(\text{CO})_4$ is as being derived from $\text{Fe}(\text{CO})_5$ by removing an equatorial CO, and the two axial CO ligands bending toward the missing CO. We therefore refer to the two kinds of CO groups as axial and equatorial. Daniel *et al.*⁴² have extensively studied the photodissociation mechanisms of $\text{Fe}(\text{CO})_5$ at a qualitative level of theory, and obtain a 3B_2 ground state for $\text{Fe}(\text{CO})_4$ with a 1A_1 state lying about 19 kcal/mol higher in energy. We also find the ground state to be 3B_2 and optimize the structure with the Fe–C–O angles constrained to be 180°. The geometry is in reasonable agreement with the experimental estimate of 145° and 120° for the bond angles.⁴¹ From the total binding energy of $\text{Fe}(\text{CO})_4$, we compute a first bond dissociation energy of $\text{Fe}(\text{CO})_5$ of 23.9 kcal/mol. Daniel *et al.*⁴² obtained 42 kcal/mol for this quantity, although their value probably

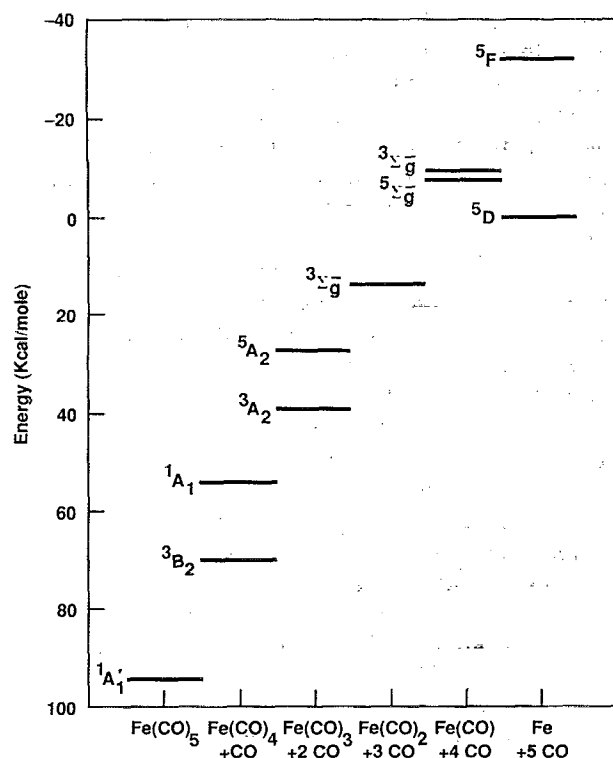


FIG. 1. The relative energetics for the $\text{Fe}(\text{CO})_n$ systems. The zero of energy is ground state Fe atom and five ground state CO molecules.

suffers from superposition error due to the use of a basis which is single ζ in the core region. Ziegler *et al.*³² calculate a value of 44 kcal/mol for the first bond dissociation energy, relative to the singlet excited state. Experimentally, Engelking and Lineberger⁸ derived a value of 55 ± 12 kcal/mol for the first CO binding energy in $\text{Fe}(\text{CO})_5$, whereas Lewis *et al.*⁹ measured a value of 41 ± 2 kcal/mol at 298 K, or 39 ± 2 kcal/mol at 0 K.⁴³ We note also that Pignataro and Lossing⁴⁴ estimate a value of 16 ± 7 kcal/mol based on the appearance potential and ionization potential of $\text{Fe}(\text{CO})_4$ in electron impact and thermal decomposition experiments on $\text{Fe}(\text{CO})_5$. However, the value of Lewis *et al.* is probably the most reliable. As discussed by Lewis *et al.*, the value of Engelking and Lineberger should be taken relative to the triplet ground state of $\text{Fe}(\text{CO})_4$, whereas their value should be taken relative to the singlet excited state. Thus there is an inconsistency between the two values, since the value of Lewis *et al.* should be the larger of the two. In order to compare with Lewis *et al.*, we also

TABLE V. Summary of the $\text{Fe}(\text{CO})_3$ results. The bond lengths r are in a_0 , the bond angle is in degrees, and the total CO binding energy BE is in kcal/mol.

	$r(\text{Fe}-\text{C})$	$r(\text{C}-\text{O})$	\angle^a	BE
3A_2	3.60	2.23	21	39.4
5A_2	3.71	2.22 ^b	15	27.6

^aThe angle is the bend out of the plane.

^b $r(\text{C}-\text{O})$ is not optimized.

performed a coarse optimization of the 1A_1 state of $\text{Fe}(\text{CO})_4$. In this case each parameter is optimized once, assuming no coupling with the other parameters, starting from the triplet-state geometry. As this single pass optimization only lowered the singlet by 2.9 kcal/mol relative to the triplet state, no additional optimizations were performed and it seems safe to conclude that the singlet state is about 15 ± 5 kcal/mol above the triplet state. This would result in our best estimate of 39 ± 5 kcal/mol for the first bond dissociation energy of $\text{Fe}(\text{CO})_5$, relative to the singlet excited state, which is in good agreement with the experimental value of Lewis *et al.* and the theoretical value of Ziegler *et al.*³² We note that while the MCPF method does not lead to an accurate total binding energy for $\text{Fe}(\text{CO})_5$, the difference in CO binding energy between $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4$ is quite well described. This is probably due to a cancellation of errors—the 3d populations for $\text{Fe}(\text{CO})_5$ and both the triplet and singlet states of $\text{Fe}(\text{CO})_4$ are quite similar, indicating that the errors which cause the low binding energies in each case are probably similar. Finally, it seems that the experimental binding energy of Engelking and Lineberger⁸ and the theoretical results of Daniel *et al.* are probably too large.

Considering now $\text{Fe}(\text{CO})_3$, we have optimized two states with the constraint of C_{3v} symmetry, which is known experimentally.⁴⁵ The lowest triplet state is found to be the 3A_2 arising from an $11e^2$ occupation. The lowest quintet state is the 5A_2 with the $12a|13a|11e^2$ occupation. The lowest singlet state was significantly higher in energy and its study was not pursued. The optimal geometries of the 3A_2 and 5A_2 states are given in Table V. These were optimized with the constraint that $\angle(\text{Fe}-\text{C}-\text{O}) = 180.0^\circ$. As the 5A_2 was found to be about 12 kcal/mol above the triplet, we did not optimize $r(\text{C}-\text{O})$. While the 5A_2 state calculations were straightforward with the MCPF method, severe convergence problems were encountered for the 3A_2 state calculations. As a result, the optimized geometry is probably somewhat less accurate than for the other systems. The convergence difficulties are due to the presence

TABLE IV. Summary of the $\text{Fe}(\text{CO})_4$ results. The bond lengths r are in a_0 , the bond angles are in degrees, and the total CO binding energy BE is in kcal/mol.

	Axial			Equatorial			BE
	$r(\text{Fe}-\text{C})$	$r(\text{C}-\text{O})$	$\angle(\text{C}-\text{Fe}-\text{C})$	$r(\text{Fe}-\text{C})$	$r(\text{C}-\text{O})$	$\angle(\text{C}-\text{Fe}-\text{C})$	
3B_2	3.550	2.210	150	3.562	2.220	104	70.3
1A_1	3.609	2.232	151	3.543	2.226	125	54.1

of two SCF solutions, so that the MCPF approach is not entirely suitable. The two SCF occupations can be described as $12a_1^2 13a_1^0$ and $12a_1^0 13a_1^2$ which is consistent with the low-lying 5A_2 state occupation. Despite these problems with the MCPF treatment of the 3A_2 state we feel that the total binding energy should be fairly reliable. Our computed value is 39.4 kcal/mol, giving a second CO binding energy for $\text{Fe}(\text{CO})_2$ of 31 kcal/mol. This is very different from the experimental value 4.6 ± 9.2 kcal/mol.⁸ We note that Waller and Hepburn⁶ suggest a value of around 20 kcal/mol for this quantity, based on a combination of the results of Engelking and Lineberger⁸ and those of Lewis *et al.*⁹ However, using the result of Lewis *et al.*, Venkataraman *et al.*⁷ have obtained sequential bond dissociation energies for $\text{Fe}(\text{CO})_2$ via a fitting procedure to their experimental data. They obtain only 10 kcal/mol for the second bond dissociation energy, significantly less than our value but reasonably consistent with the value of Engelking and Lineberger. In spite of the limitations of our calculations, a 20 kcal/mol error for the second CO binding energy seems to be surprisingly large.

We now consider the results for FeCO and $\text{Fe}(\text{CO})_2$. Based on other monocarbonyl species, FeCO is expected to be linear, and there are infrared studies which indicate a linear structure for $\text{Fe}(\text{CO})_2$,⁴⁶ so we consider only linear structures for these molecules in the current work. The qualitative bonding in FeCO has been analyzed in detail previously using the constrained space orbital variation (CSOV) method⁴⁷ at the complete-active-space SCF (CASSCF) level. In the current work we are more interested in the binding energies and ground state assignment, so we do not give a detailed description of the bonding in either FeCO or $\text{Fe}(\text{CO})_2$. (We note that the bonding in several other transition metal mono- and dicarbonyl species has been recently studied in some detail.)³⁰ Barbier *et al.*⁴⁸ have studied the FeCO molecule using the CIPSI CI method. They found the ground state to be $^3\Sigma^-$, with a $^5\Sigma^-$ state some 12 kcal/mol higher in energy. Although these states were bound with respect to their dissociation asymptotes (by 35.9 and 15.9 kcal/mol, respectively), they were unbound with respect to the Fe ground state and ground state CO (by 18.1 and 29.9 kcal/mol, respectively). In later work⁴⁹ these authors again found $^3\Sigma^-$ ground state for FeCO , with a higher lying $^5\Sigma^-$ state, which were bound asymptotically, but they did not indicate the binding relative to the Fe ground state. We considered the $^5\Sigma^-$, $^3\Sigma^-$, and $^3\Delta$ states of FeCO , and the $^5\Sigma_g^-$, $^3\Sigma_g^-$, and $^3\Delta_g$ states of $\text{Fe}(\text{CO})_2$. The quintet states are derived from the $3d^7 4s^1(^5F)$ first excited state of the Fe atom, which lies 20 kcal/mol above the $3d^6 4s^2(^5D)$ ground state, whereas the triplet states are derived from the $3d^7 4s^1(^3F)$ state, which lies 34 kcal/mol above the ground state.⁵⁰ Our results are presented in Table VI.

For FeCO , we find that the $^5\Sigma^-$ and $^3\Sigma^-$ states are very close in energy, with the $^5\Sigma^-$ state lowest without the relativistic correction, but the $^3\Sigma^-$ state being slightly lower when the relativistic correction is included. The relativistic correction has only a small effect on the geometries and energetics, however. The $^3\Delta$ state lies much

TABLE VI. Summary of geometries (a_0), excitation energies (kcal/mol), and binding energies (kcal/mol) of FeCO and $\text{Fe}(\text{CO})_2$.^a

	$r(\text{Fe-C})$	$r(\text{C-O})$	ΔE	BE
FeCO				
$^5\Sigma^- (\sigma^1 \sigma'^1 \delta^2 \pi^4)$	3.620	2.250	0.0	-7.5
	3.574	2.254	0.5	...
$^3\Sigma^- (\sigma^2 \delta^2 \pi^4)$	3.250	2.286	1.6	...
	3.245	2.285	0.0	-9.8
$^3\Delta (\sigma^1 \delta^3 \pi^4)$	3.414	2.285	24.5	...
	3.370	2.287	27.0	...
$\text{Fe}(\text{CO})_2$				
$^5\Sigma_g^- (\sigma_g^2 \delta_g^2 \pi_g^4)$	3.625	2.216	0.0	14.0
	3.597	2.216	0.0	12.2
$^3\Delta_g (\sigma_g^1 \delta_g^3 \pi_g^4)$	3.579	2.234	14.7	...
	3.551	2.236	16.2	...
$^5\Sigma_g^- (\sigma_g^1 \sigma'_g \delta_g^2 \pi_g^4)$	4.761	2.200	50.5	...
	4.656	2.203	54.0	...

^aThe second line of each entry includes the relativistic correction.

higher in energy. These results are in contrast to those of Barbier *et al.* who found the $^3\Sigma^-$ state to be significantly lower in energy than the $^5\Sigma^-$ state. However, the $^3\Sigma^-$ state appears to have significantly more multi-reference character than the $^5\Sigma^-$ state, so the single-reference MCPF method may be biased against the $^3\Sigma^-$ state. In accord with Barbier *et al.*, we find that both states are unbound with respect to the Fe atomic ground state but bound quite strongly with respect to their dissociation asymptotes (by 34 kcal/mol for the $^3\Sigma^-$ state and 24 kcal/mol for the $^5\Sigma^-$ state).

To explore possible errors in the computed binding energy of FeCO in more detail, we have carried out additional calculations on the $3d^6 4s^2(^5D)$, $3d^7 4s^1(^5F)$, and $3d^7 4s^1(^3F)$ states of the Fe atom. The quintet states may be treated with the MCPF approach, for which we find that the 5F state is around 12 kcal/mol too high in energy. For the 5D - 3F separation, we have used the CASSCF/averaged CPF (ACPF)⁵¹ procedure, the multireference analogue of SCF/MCPF. We find that this separation is also too large by about 12 kcal/mol (Note: the 5D - 5F separation is also around 12 kcal/mol too large at the CASSCF/ACPF level of treatment.) These results imply that the binding energy will be around 12 kcal/mol larger for either the $^5\Sigma^-$ or $^3\Sigma^-$ states if we took the molecules to their dissociation asymptotes and used the experimental separation to refer the result to ground state Fe atoms. However, even if this is done, the FeCO binding energy is still very small, around 5 kcal/mol. Experimentally, Engelking and Lineberger⁸ find a value of 23 ± 7 kcal/mol for the binding energy of Fe-CO . Venkataraman *et al.*⁷ obtain an upper bound of 39 kcal/mol from their fitting procedure, which is consistent with the value of Engelking and Lineberger. As an additional check, we carried out MCPF calculations on the $^5\Sigma^-$ and $^3\Sigma^-$ states of FeCO using a large atomic natural orbital⁵² basis set for both Fe and CO. Again, both states are unbound with respect to the Fe ground state, by 3.8 and 5.6 kcal/mol, respectively. Thus the basis set does not appear to be a limiting factor. Another possible explanation for the discrepancy between experiment and theory is

that the experimental results are relative to an excited Fe atomic asymptote. For example, if dissociation were to the 5F state of Fe, the computed dissociation energy would be around 18 kcal/mol, consistent with the experimental results.

Moving on to $\text{Fe}(\text{CO})_2$, the additional repulsion from the second CO ligand causes the $^5\Sigma_g^-$ state to be very weakly bound asymptotically, some 50 kcal/mol above the $^3\Sigma_g^-$ ground state. The $^3\Delta_g$ state is relatively lower in energy than the analogous state in FeCO , an effect again due to the additional Fe–CO repulsion in the dicarbonyl. As for FeCO , the binding energy is quite low relative to the Fe atomic ground state, and correcting for the error in the triplet–quintet separation of the Fe atom will only increase this to around 25 kcal/mol. However, using the FeCO results, the bond dissociation energy of a single CO in $\text{Fe}(\text{CO})_2$ is found to be 22 kcal/mol, in good agreement with the value of Engelking and Lineberger,⁸ 23 ± 7 kcal/mol. Thus as for $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4$, it appears that the difference in binding energies between $\text{Fe}(\text{CO})_2$ and FeCO is quite well described. We note that Venkataraman *et al.*⁷ obtain a lower bound of 27 kcal/mol for this value, which is reasonably consistent with the current results. From the $\text{Fe}(\text{CO})_2$ and $\text{Fe}(\text{CO})_3$ results, we obtain the bond dissociation energy of CO from $\text{Fe}(\text{CO})_3$ as 25 kcal/mol, compared with 32 ± 7 kcal/mol from Engelking and Lineberger, or 25 kcal/mol from the fitting procedure of Venkataraman *et al.*

IV. CONCLUSIONS

There are clearly problems associated with the calculation of both the total $\text{Fe}-(\text{CO})_n$ binding energies of the various $\text{Fe}(\text{CO})_n$ species and the relative binding energies for the sequential removal of a single CO ligand from the various species. As discussed previously, at the MCPF level we are underestimating the strength of the metal–CO bond and are therefore not able to overcome the promotion and loss of exchange energy. Estimation of the error associated with the calculation is difficult, since it comes from various sources—errors in the description of the atomic asymptotes, basis set errors, errors due to the multi-reference nature of particular states and so on. Some of these errors scale with the number of CO ligands, whereas others do not. However, despite these problems, it seems that the equilibrium properties of the saturated $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$ species, such as bond lengths and force constants, are calculated quite well with the MCPF approach. In addition, we may fairly confidently give the following estimate of the sequential bond dissociation energies of CO from $\text{Fe}(\text{CO})_5$: 39, 31, 25, 22, and > 5 kcal/mol, respectively. These results are in reasonable agreement with experimental data. We note that the first bond dissociation energy is relative to the singlet ground state of $\text{Fe}(\text{CO})_5$ and the lowest singlet state of $\text{Fe}(\text{CO})_4$, whereas the second is relative to the ground triplet states of $\text{Fe}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3$. Also the last value, the binding energy for FeCO , would be modified to 18 kcal/mol if dissociation occurred to the $\text{Fe}(^5F)$ excited state asymptote.

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