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Accurate *ab initio* calculations have been completed on $Cr(CO)_6$, $Cr(CO)_5$ and free CO. Binding energies, geometries, force constants were computed and compared to experimental data. This has been written up as the paper entitled "The structure and energetics of $Cr(CO)_6$ and $Cr(CO)_5$" by L. A. Barnes, B. Liu and R. Lindh, and will be submitted to the Journal of Chemical Physics for publication. Copies of the paper are enclosed with this report.

The density functional program deMon is being used to investigate the application of different density functional approaches to the structure and energetics of small boron clusters. To calibrate the density functional results, *ab initio* MCSCF calculations are also being carried out and compared to the density functional results. For the cluster B_5, initial results indicate that the density functional methods are giving results significantly better than SCF, with results of similar quality to the MCSCF calculations. Once these calibration calculations are concluded, larger clusters will be investigated with the density functional approach.

The structure and energetics of $Cr(CO)_6$ and $Cr(CO)_5$

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Abstract

The geometric structure of $Cr(CO)_6$ is optimized at the modified coupled-pair functional (MCPF), single and double excitation coupled-cluster (CCSD) and CCSD(T) levels of theory (including a perturbational estimate for connected triple excitations), and the force constants for the totally symmetric representation are determined. The geometry of $Cr(CO)_5$ is partially optimized at the MCPF, CCSD and CCSD(T) levels of theory. Comparison with experimental data shows that the CCSD(T) method gives the best results for the structures and force constants, and that remaining errors are probably due to deficiencies in the one-particle basis sets used for CO. A detailed comparison of the properties of free CO is therefore given, at both the MCPF and CCSD/CCSD(T) levels of treatment, using a variety of basis sets. With very large one-particle basis sets, the CCSD(T) method gives excellent results for the bond distance, dipole moment and harmonic frequency of free CO. The total binding energies of $Cr(CO)_6$ and $Cr(CO)_5$ are also determined at the MCPF, CCSD and CCSD(T) levels of theory. The CCSD(T) method gives a much larger total binding energy than either the MCPF or CCSD methods. An analysis of the basis set superposition error (BSSE) at the MCPF level of treatment points out limitations in the one-particle basis used here and in a previous study. Calculations using larger basis sets reduce the BSSE, but the total binding energy of $Cr(CO)_6$ is still significantly smaller than the experimental value, although the first CO bond dissociation energy of $Cr(CO)_6$ is well described. An investigation of $3s3p$ correlation reveals only a small effect. The remaining discrepancy between the experimental and theoretical total binding energy of $Cr(CO)_6$ is probably due to limitations in the one-particle basis, rather than limitations in the correlation treatment. In particular an additional d function and an f function on each C and O are needed to obtain quantitative results. This is underscored by the fact that even using a very large primitive set (1042 primitive functions contracted to 300 basis functions), the superposition error for the total binding energy of $Cr(CO)_6$ is 22 kcal/mol at the MCPF level of treatment.

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1 Introduction

The calculation of accurate binding energies for the transition metal carbonyl systems remains a challenging problem for *ab initio* quantum chemistry. These systems are of great interest in many areas of chemistry, ranging from organometallic synthesis to catalysis, surface chemistry, photophysics and thin film deposition of metals (see, for example, references [1, 2, 3] and references therein). The average bond dissociation energy is well known for several saturated transition metal carbonyl systems such as $Ni(CO)_4$, $Fe(CO)_5$, and $Cr(CO)_6$, but individual carbonyl binding energies are harder to determine experimentally. However, it is the individual bond energies which may be more important in understanding the different processes occurring chemically (see, for example, references [4, 5] and references therein).

From a theoretical viewpoint, the total metal carbonyl binding energy is an important quantity since it provides a good calibration of the theoretical methodology. If this quantity can be computed accurately then individual metal carbonyl binding energies may also be predicted with some confidence. However, if the total binding energy is not well determined, then there may be problems when computing individual binding energies. In addition, the geometrical structure and vibrational frequencies (or force constants) of the saturated carbonyl species are known in several cases, providing another useful calibration of the methods.

Previously, the modified coupled-pair functional (MCPF) method [6] was used to study the systems $Ni(CO)_n$, $n = 1, 4$ [7], $Fe(CO)_n$, $n = 1, 5$ [4] and $Cr(CO)_6$ [4], providing the best *ab initio* binding energies at that time. In general, the total binding energies are too low at this level of treatment — 82% of the experimental value for $Ni(CO)_4$ and only 67% and 68% of the experimental value for $Cr(CO)_6$ and $Fe(CO)_5$, respectively. For $Fe(CO)_5$ the first bond dissociation energy was well determined, whereas subsequent bond dissociation energies were harder to determine, so that only a lower bound of 5 kcal/mol could be given for the last bond dissociation energy. In contrast, the bond distances and force constants were generally in better agreement with the experimental data than would be expected on the basis of the binding energies alone. For the cases of $Fe(CO)_5$ and $Cr(CO)_6$ the possible sources of error in the binding energies were discussed in terms of the difficulty in accurately describing the change in metal $3d$ configuration upon forming the carbonyl complex and the loss of the high-spin coupling exchange energy in the molecule.

Recently, the single and double excitation coupled-cluster (CCSD) method that includes a perturbational estimate for connected triple excitations (T) [8] has been used to study Ni(CO)$_n$, $n = 1, 4$, and Ni(C_2H_4) [9]. This CCSD(T) approach yielded good results in all cases, giving an additional 17.5 kcal/mol of binding energy for Ni(CO)$_4$ compared with the MCPF result. After correction for basis set superposition error (BSSE), the total binding energy of Ni(CO)$_4$ was 89% of the experimental value. The remaining errors were shown to be largely due to deficiencies in the one-particle basis set, because use of a very large one-particle basis set for yielded an additional 3.5 kcal/mol in the binding energy. If this correction is applied to Ni(CO)$_4$ (for each CO), the experimental result would be reproduced almost exactly.

In the previous work [4], we compared the results of the MCPF calculations to other theoretical work, such as Xα [10], density functional [11] and SDCI calculations [12]. A detailed analysis of the energetics and electronic structure of Cr(CO)$_6$ was recently carried out by Kunze and Davidson [13], at the SCF level of theory in a large one-particle basis set. However, even in a large one-particle basis set, at the SCF level of treatment Cr(CO)$_6$ is still unbound by 111 kcal/mol [13] relative to the ground state Cr and CO fragments, illustrating the importance of electron correlation for the total binding energy. Regarding Cr(CO)$_5$ and the first bond dissociation energy of Cr(CO)$_6$, there is some previous work which has been carried out at a qualitative level in small basis sets. We note in particular the work of Hay [14] on different electronic states of Cr(CO)$_5$ and Sherwood and Hall [15] on the dissociation of a single carbonyl from Cr(CO)$_6$. In the former work, SDCI calculations in a small one-particle basis at fixed bond lengths found Cr(CO)$_5$ to have a $^1A_1$ ground state of C_{4v} symmetry (square pyramid). The D_{3h} structure (trigonal bipyramid) was about 9 kcal/mol higher in energy. The latter work found the first bond dissociation energy of Cr(CO)$_6$ to be 49.8 kcal/mol at the SCF level of theory. In addition, Demuynck *et al.* [16] have studied the interaction of a rare-gas atom with Cr(CO)$_5$, at the SCF level of theory in small basis sets, using experimental bond distances from Cr(CO)$_6$. They found the ground state of Cr(CO)$_5$ to be $^1A_1$ in C_{4v} symmetry, with an equatorial to axial CO angle of around 92°. More recently, Pacchioni [17] has carried out some SCF calculations on Cr(CO)$_5$ in a study of Cr(CO)$_5$H$_2$ and Cr(CO)$_4$(H$_2$)$_2$, and Nilson *et al.* [18] have carried out some limited MCSCF calculations in a combined experimental and theoretical study of the the photoelectron spectrum of Cr(CO)$_6$. However, these studies did not address the binding energies or geometric structures of Cr(CO)$_5$ or Cr(CO)$_6$.

In the current work we have used the MCPF, CCSD and CCSD(T) approaches to study Cr(CO)$_6$ and Cr(CO)$_5$ in the same basis as used previously [4] and in significantly larger basis sets at the MCPF level of treatment only. The geometric structure of $Cr(CO)_6$ is optimized at the CCSD and CCSD(T) levels of theory and the force constants for the totally symmetric representation are determined. The previously published work which gave the structure and Cr–C totally symmetric force constant of $Cr(CO)_6$ using the MCPF approach is extended to include the C–O totally symmetric force constant and the coupling term. The geometry of $Cr(CO)_5$ is partially optimized at the MCPF, CCSD and CCSD(T) levels of theory.

The first bond dissociation energy, that is the energy required for the process

$$\mathrm{Cr(CO)_6} \rightarrow \mathrm{Cr(CO)_5} + \mathrm{CO} \tag{1}$$

is known experimentally, as well as the total binding energy of $Cr(CO)_6$, the energy required for the process

$$\mathrm{Cr(CO)_6} \rightarrow \mathrm{Cr} + 6\mathrm{CO} \tag{2}$$

We have looked at both these processes in the current work, including a correction for BSSE and the effect of semi-core $3s3p$ correlation.

Since many of the differences between the experimental and theoretical results (especially in the structures and force constants) can be rationalized in terms of deficiencies in the treatment of free CO, results for some of the properties of free CO at the MCPF, CCSD and CCSD(T) levels of theory are given, in a variety of one-particle basis sets.

In § 2 we discuss the methods used, including the one-particle and n-particle treatments. In § 3 we present the results and discussion, first giving the free CO results (§ 3.1), then the geometrical structure and force constants for $Cr(CO)_6$ (§ 3.2), the geometrical structure for $Cr(CO)_5$ (§ 3.3), and finally the results for the bond dissociation energies (§ 3.4).

2 Methods

The standard Cr basis is the ($14s$ $9p$ $5d$) primitive Gaussian basis set of Wachters [19], contracted to [$8s$ $4p$ $3d$] using his contraction scheme 2. Two diffuse p functions, as recommended by Wachters, and the diffuse d function of Hay [20] are added, yielding a final basis set of the form ($14s$ $11p$ $6d$)/[$8s$ $6p$ $4d$]. The standard C and O basis sets are [$4s$ $3p$] contractions of the ($9s$ $5p$) primitive Gaussian set of van Duijneveldt [21], with the s and p spaces contracted (5211) and (311) respectively. In all calculations, except those done using CADPAC (see below), only the pure spherical harmonics are used.

For the study of free CO, and for the larger basis set calculations on $Cr(CO)_6$ and $Cr(CO)_5$, we use a $(13s\ 8p\ 6d\ 4f\ 2g)$ primitive basis set for C and O, contracted using the Atomic Natural Orbital (ANO) procedure [22]. These basis sets are derived from the (13s 8p) sets of van Duijneveldt [21] supplemented with polarization functions as prescribed in reference [22]. This is supplemented with a single h function with exponent 1.24 for C and 2.21 for O, and a diffuse set of s, p and d functions, with exponents 0.040, 0.028 and 0.027 for C and 0.075, 0.050 and 0.052 for O. This primitive set is contracted in a variety of ways, ranging from $[4s\ 3p\ 1d]$ for use in $Cr(CO)_6$ and $Cr(CO)_5$, to $[6s\ 5p\ 4d\ 3f\ 2g\ 1h]+(1s\ 1p\ 1d)$ for use in free CO when both the h function and the diffuse s, p and d set is included.

For the valence correlation calculations on $Cr(CO)_6$ and $Cr(CO)_5$ we have used two basis sets which we term "small" and "large". The "small" basis set consists of the standard Wachters and van Duijneveldt sets described above and is the same basis used previously [4], containing 202 contracted functions for $Cr(CO)_6$. We use this basis set to compare results at the MCPF, CCSD and CCSD(T) levels of treatment. The "large" basis set is the Wachters metal set supplemented with a $(3f)/[1f]$ contracted function (see reference [23]), and the $[4s\ 3p\ 1d]$ ANO set on C and O, giving 265 contracted basis functions for $Cr(CO)_6$. With this basis set we use only the MCPF method, relying on the small basis set results to give qualititive trends which can be used to estimate results in the large basis for the other methods.

It is well known that all the valence electrons must be correlated in metal-carbonyl complexes in order to compute accurate binding energies [7, 24]. However, as discussed by Kunze and Davidson [13], in $Cr(CO)_6$ there is a significant overlap between the CO 5σ electrons and the $3p$ electrons of Cr. Therefore, we have also investigated the effect of correlating the chromium semi-core $3s3p$ electrons *and* all the valence electrons in $Cr(CO)_6$. We denote the calculations as "valence only" if only the valence electrons were correlated, or "$3s3p$ + valence" if both the $3s3p$ and valence electrons are correlated.

For the $3s3p$ + valence calculations we initially used a basis set derived from the "small" set discussed above, with the inner $3p$ functions on Cr more flexibly contracted and the addition of two contracted f functions to Cr, but retaining the $[4s\ 3p]$ segmented basis set on CO. However, due to the unbalanced nature of this basis, the superposition error was increased considerably and the binding energies were anomalous. Therefore, we instead used the $(20s\ 12p\ 9d)$ primitive set of Partridge [25], optimized for the ^5D state of Cr. This was contracted in a flexible way to $[3+6s\ 2+4p\ 1+4d]$, with the outermost six s, four p and four d functions uncontracted. The inner three s, two p and one d functions are generally contracted based on the $1s$, $2s$, $3s$, $2p$, $3p$ and $3d$ SCF atomic orbitals, respectively. This basis is supplemented with two even-tempered diffuse p functions to describe the $4p$ orbital, with exponents of 0.127803 and 0.051121, and a diffuse d function with exponent 0.045794 [25]. In addition, we use a $(4f)/[3f]$ set of functions, based on the $(3f)$ primitive set of the "large" basis referenced above and a $(1f)$ primitive function optimized for $3p$ correlation in the Cr atom [26]. The contraction coefficients are taken from the natural orbitals of an MCPF calculation on the ^7S state of the Cr atom which correlates the $3s$, $3p$, $3d$ and $4s$ electrons. The final Cr basis is of the form $(20s\ 14p\ 10d\ 4f)/[3{+}6\text{s}\ 2{+}6\text{p}\ 1{+}5\text{d}\ 3\text{f}]$ and is combined with the $[4s\ 3p\ 1d]$ ANO basis set for CO to give the "large 3s3p" basis set for $Cr(CO)_6$. This basis consists of 1042 primitive Gaussian functions and 300 contracted functions.

As discussed above, the MCPF, CCSD and CCSD(T) methods are used, correlating 56 electrons in $Cr(CO)_5$ and 66 electrons for the valence correlation treatment of $Cr(CO)_6$, or 74 electrons when $3s3p$ correlation is included. As noted in previous work, the use of a size-extensive method is essential when treating this many electrons in the correlation procedure. The reference function is an SCF single configuration computed with full symmetry and equivalence restrictions. For the CCSD/CCSD(T) calculations on the ^{7}S state of the Cr atom we use the open-shell coupled-cluster method [27] to compute the atomic energy used in the binding energy calculation for the (closed shell) molecular species.

For $Cr(CO)_6$ we consider only the $^1A_{1g}$ state with $3d$ occupation t_{2g}^6 in O_h symmetry. At the SCF level of theory the geometry was optimized using analytic gradient techniques (using the small basis), under the constraint of O_h symmetry, and harmonic frequencies were computed. At the correlated level the geometry was optimized by fitting energy points with displacements of 0.025 a_0 in the Cr–C bond and 0.010 a_0 in C–O, first performing independent Cr–C and C–O displacements, and then combined displacements to determine coupling effects. In general, about 14 points were used to determine the two bond lengths and three force constants for the totally symmetric representation (see reference [28], Table IX, for a definition of the symmetry internal coordinates and force constants).

Experimentally, matrix-isolated $Cr(CO)_5$ has been shown to be of C_{4v} symmetry, obtained from $Cr(CO)_6$ by the removal of a single CO moiety without further geometrical rearrangement (see references [29]–[33]). This gives a $^1A_1$ state with occupation $e^4b_2^2$. There is also a D_{3h} structure (analogous to Fe(CO)$_5$) which has a $^3A_2'$ ground state with $e''^4e'^2$ occupation (see the work of Hay [14] for a general discussion of the electronic structure of Cr(CO)$_5$). Both structures were fully optimized at the SCF level of theory in the small basis, and were found to be almost degenerate, with the C_{4v} structure lower by only 0.8 kcal/mol. Previously, Hay [14] found the D_{3h} structure to be lower by 2.8 kcal/mol, at the SCF level of theory, with a minimal basis on CO (and without geometry optimization). Using a larger [$3s$ $2p$] CO basis (also without full geometry optimization) Demuynck *et al.* [16] found the C_{4v} structure to be lower by around 10 kcal/mol at the SCF level of theory. In addition, at the SDCI level the C_{4v} structure was lowered by around 12 kcal/mol [14] compared to the D_{3h} structure. Therefore, in the current work only the C_{4v} structure was further (partially) optimized including electron correlation at the MCPF, CCSD and CCSD(T) levels of theory. The bond angles were fixed at the SCF values and the C–O distances were fixed at a value deduced from a combination of the SCF optimized values and the correlated results for Cr(CO)$_6$ (see § 3.2 and § 3.3 later). The Cr–C bonds may be separated into "axial" and "equatorial", with the axial bond along the C_4 axis. For the CCSD and CCSD(T) methods only the equatorial bond distance was optimized, the axial distance again being fixed at a value derived from the SCF results for Cr(CO)$_5$ and Cr(CO)$_6$ and the correlated results for Cr(CO)$_6$. We note that the binding energy is relatively insensitive to the Cr–C bond distance and the bond angles.

For free CO, the equilibrium bond distance (r_e) and force constant (k) were determined by fitting energy points with displacements of 0.005 a_0 about the equilibrium point, using an expansion in r up to r^4. The harmonic frequency (ω_e) was computed from the force constant using atomic masses of 12.0 amu for C and 15.9949141 amu for O. The dipole moments ($\mu_{\rm ff}$) were determined via a finite field (energy derivative) approach, fitting field points in steps of ± 0.001 a.u. in the field at the equilibrium geometry. The accuracy in the fit is expected to be about 0.00001 a_0 in r_e, 0.00001 a.u. in μ, 0.0001 aJ/Å^2 in the force constant k and 0.2 cm^{-1} in the harmonic frequency ω_e. For the SCF and MCPF approaches, dipole moments ($\mu_{\rm ex}$) were also determined as an expectation value. The most important relativistic corrections (the mass-velocity and Darwin terms) were included in certain cases using first-order perturbation theory [34, 35].

The calculations were performed on an IBM3090/300J and IBM RISC SYSTEM/6000 computers at the IBM Almaden Research Center, and on the the NASA Ames Central Computer Facility and NAS facility CRAY Y–MP computers. The

SCF geometry optimizations and harmonic frequency calculations on $Cr(CO)_5$ and $Cr(CO)_6$ were performed using the CADPAC [36] program system. The integrals for the correlated calculations were evaluated with the MOLECULE [37] and SEWARD [38] programs. The SCF/MCPF calculations were performed using the SWEDEN [39] program system, and the closed shell CCSD/CCSD(T) calculations were performed using the TITAN [40] program system. The open-shell CCSD/CCSD(T) calculations were performed using the code of Scuseria [27].

3 Results and Discussion

3.1 Free CO results

In order to understand some of the deficiencies in the results for $Cr(CO)_6$ and $Cr(CO)_5$ it is necessary to first look at the treatment of free CO with the current theoretical methods as a function of one-particle basis set size. In Table 1 we present results for free CO in a variety of basis sets, at the MCPF, CCSD and CCSD(T) levels of treatment.

The [4*s* 3*p*] segmented basis set gives results which are generally in poor agreement with the experimental data [41, 42]. At the SCF level, the bond length is too short and the harmonic frequency is almost 100 cm^{-1} too large (and consequently, the force constant is too high). The dipole moment has the wrong sign, as is well known, but more importantly is much too large in magnitude. All three correlation treatments increase the bond length and reduce the frequency significantly. However, the bond length is now in worse agreement with experiment than the SCF results. The dipole moment is significantly improved compared to the SCF results, which is an encouraging result, although still of the wrong sign when computed using the finite field approach. It is interesting to note the difference between the finite field result (μ_{ff}) and the expectation value (μ_{ex}) for the MCPF approach. In the previous work [4] we had only compared with experiment for the expectation value, which is a misleading result.

The [4*s* 3*p* 1*d*] ANO basis set gives significantly better results — the bond length and frequency are much closer to experiment, and the dipole moment is very good, especially at the CCSD(T) level (we do not consider the SCF results any further). Most of the improvement here is probably due to the addition of the *d* function rather than due to the larger primitive set — for example, adding a single *d* function on C and O to the [4*s* 3*p*] segmented basis gives r_e=2.154 a_0 and μ_{ex}=0.092 a.u. at the MCPF level of theory [43], fairly close to the ANO basis set results.

Expanding the basis to [4*s* 3*p* 2*d* 1*f*] improves the frequency and bond distance once more but the dipole moment is in slightly worse agreement with experiment, for all three methods. The dipole moment seems to have converged reasonably well with respect to basis set at this point, whereas the bond distance and frequency are still sensitive to basis set.

With the [5*s* 4*p* 3*d* 2*f* 1*g*] basis set, the bond distance is again reduced and the frequency increased, by about the same amount as the change from the previous two basis sets, and the dipole moment is once again reduced by a small amount. However, at this point we see that the CCSD and MCPF approaches give bond distances which are shorter than experiment and a frequency which is too large, with the MCPF approach being superior. The CCSD(T) approach is still further away from experiment than MCPF for the bond distance, but the frequency is in much better agreement, as is the dipole moment.

Uncontracting the outermost primitive functions to give the $[5+1s\ 4+1p\ 3+1d\ 2+1f\ 1+1g]$ basis has a small but significant effect on the properties — the bond distance decreases slightly, the frequency is marginally higher, and the dipole moment increases, for all three methods. The CCSD(T) results move closer to experiment with all these changes and the results appear to be well converged with respect to basis set for all the methods. In order to confirm the basis set convergence and explore the remaining small differences with experiment, we now consider some additional basis set expansions.

We start with a [6*s* 5*p* 4*d* 3*f* 2*g*] basis set — this is the same size as the $[5+1s\ 4+1p\ 3+1d\ 2+1f\ 1+1g]$ set discussed above, and gives very similar properties but with a slightly lower total energy. In this basis the bond length and harmonic frequency of CO are of similar accuracy to those of N_2 [44] computed using the CCSD(T) level in a similar quality basis set.

Adding an *h* function has only a small effect — the dipole moment is decreased by about 0.0003 a.u., the bond length decreased very slightly and the frequency increased by about 3 cm^{-1}. The CCSD(T) frequency is now very close to experiment. At this point we have included an estimate of relativistic effects via a perturbation correction to the MCPF results — the effect is small, but of the same order as the effect of the *h* function. The frequency is reduced very slightly with the relativistic correction. We note that the ANO procedure can introduce a large contraction error for this type of relativistic correction [45], but the effects will probably be small here in any event.

Finally, we add the diffuse *spd* set of functions. This has almost no effect on the bond distance or frequency — however, the dipole moment is increased by about 0.001 a.u., a small but significant effect. The best results overall are with the CCSD(T) method — the bond distance is about 0.005 a_0 too large, the dipole moment about 0.005 a.u. too small and the frequency about 6 cm^{-1} too small (including the +REL correction from MCPF). The MCPF method gives the best bond distance — however, more accurate calculations (see below) will almost certainly decrease the bond distance so that MCPF will be further from experiment. We note that the MCPF method produces results which are between CCSD and CCSD(T) in quality.

For the $Cr(CO)_6$ calculations, an ideal basis would be the [5*s* 4*p* 3*d* 2*f* 1*g*] set for CO — however, even the [4*s* 3*p* 2*d* 1*f*] basis leads to about 1300 primitives and 440 basis functions (also including a larger Cr basis), which is too large at the current time. Therefore we settle for the [4*s* 3*p*] and [4*s* 3*p* 1*d*] basis sets for use in $Cr(CO)_5$ and $Cr(CO)_6$, and demonstrate that the results are still useful given the basis set study of free CO.

There is a large amount of work in the literature on free CO, and studies on the dipole moment abound. The larger basis set studies (see, for example, references [46]–[48]) have not optimized the bond length, which is also difficult to compute accurately. Most recently, Scuseria *et al.* [48] obtained a dipole moment at a fixed geometry using the CCSD(T) method which is in excellent agreement with the experimental value (see Table 1). Part of the difference with the current work is due to the different geometry used here — an increase of 0.003–0.004 a.u. may be expected in the dipole moment computed here at the geometry of Scuseria *et al.*, based on an estimated dipole moment derivative at the MCPF level of theory (dipole moment derivatives computed using various MCSCF/CI wavefunctions are qualitatively similar to the MCPF result [49]). In addition, Scuseria *et al.* used a larger *sp* basis than that used here, with two sets of diffuse functions. Our diffuse *sp* set corresponds closely to their first *sp* diffuse set. Adding a second diffuse *spd* set to our basis may give a small effect also, although Scuseria's work indicates this should be less than 0.001 a.u. for the dipole moment. Overall, Scuseria's *sp* basis is more flexibly contracted, which may explain the small difference remaining.

The current calculations are probably among the most accurate to date on CO. To improve on these results, several factors need to be accounted for — core-core and core-valence correlation may be expected to reduce the bond distance by about 0.002–0.003 a_0 (from work on methane by Bowen-Jenkins *et al.* [50]). An improved estimate of relativistic effects may also reduce the bond distance slightly. A larger primitive set and more flexible *sp* contraction should also be considered.

3.2 The geometric structure and force constants of $Cr(CO)_6$

The bond lengths for $Cr(CO)_6$ are given in Table 2. The small basis results using the MCPF method are slightly different to those published previously [4], due to the use of a finer grid for the fitting in the current work. We note that the Cr–C distance at the SCF level is much too long, as expected, and electron correlation reduces this distance significantly. Interestingly, the CCSD approach yields a shorter bond distance than MCPF (we note that for free CO, the MCPF approach was always *between* CCSD and CCSD(T)), and adding the triples correction has a significant effect, so that the CCSD(T) method yields a Cr–C bond distance which is only about 0.05 a_0 longer than experiment [51, 52]. As found using the MCPF approach in the previous work, the C–O distance is significantly too long at the correlated level when compared to the experimental data. However, comparing the C–O bond distances in Table 1 in the [4*s* 3*p*] basis with those in Table 2, we see that the error is less than 0.01 a_0 for all three methods after correcting for basis set effects.

Using the large basis set at the MCPF level gives significantly improved results. The Cr–C distance is about 0.03 a_0 shorter and the C–O distance is 0.05 a_0 shorter, in line with the results of Table 1. Applying these changes to the CCSD(T) distances in the small basis, we estimate a value for r(Cr–C) of about 3.63 a_0 and r(C–O) of about 2.18 a_0 at the CCSD(T) level, in reasonable agreement with the experimental data. We note that in free CO, the CO bond distance decreases by 0.02 a_0 on going from the [4*s* 3*p* 1*d*] basis to the largest basis set, which accounts almost entirely for the remaining discrepancy with experiment for $Cr(CO)_6$. Thus it seems that improvements in the one-particle basis set for $Cr(CO)_6$ would yield very good agreement with experiment at the CCSD(T) level of treatment, but that even with the [4*s* 3*p*] basis the *change* in the C–O bond length on going from free CO to $Cr(CO)_6$ is well described.

The force constants for $Cr(CO)_6$ are given in Table 3, and are consistent with the bond length results discussed above. The Cr–C force constant, F_{22}, is improved on going from the MCPF level to CCSD and CCSD(T) levels of treatment, as found for r(Cr–C). In the large basis, the MCPF value for F_{22} is increased significantly so that we may estimate a value of around 2.5 aJ/Å^2 at the CCSD(T) level in the large basis, which is to be compared with the experimental value of 2.44 aJ/Å^2 [28].

The C–O force constant, F_{11}, is too small in the small basis for all three methods, consistent with the free CO results of Table 1 in the [4*s* 3*p*] basis. The force constant is smaller than in free CO, consistent with the longer bond C–O distance in $Cr(CO)_6$. In the large basis F_{11} is markedly better, mainly due to improvement in the treatment of free CO (as noted for r(C–O)), although the MCPF value is larger than experiment in the large basis. However, the CCSD(T) method yields an F_{11} value which is significantly smaller than the MCPF value in the small basis, and we may estimate a value of 18.0 aJ/Å^2 for the CCSD(T) method in the large basis, which compares well with the experimental value of 18.11 aJ/Å^2 [28].

The coupling term F_{12} is too small at all levels of theory, and interestingly is smaller in the large basis, and smaller at the CCSD(T) level than MCPF. It is difficult to predict how this term will change with higher levels of theory — however, given the relatively large error bar on the experimental value and the fact that the experimental value may be significantly affected by anharmonic effects, the results are reasonable.

Overall, the theoretical results for geometry and force constants are in good agreement with experiment within the limitations of the one-particle basis set, and the CCSD(T) method yields consistently better results than MCPF.

3.3 The geometric structure of $Cr(CO)_5$

The results for the structure of $Cr(CO)_5$ are given in Table 4, in the small basis set. As noted above, matrix-isolated $Cr(CO)_5$ is known to have C_{4v} symmetry, with an angle $\angle C_{ax}CrC_{eq}$ of about 93° [33], although the D_{3h} structure has also been proposed under certain conditions [53] (see also reference [33]). No gas-phase structural information is known.

We first look briefly at the D_{3h} structure in Table 4. This is the same structure as found for $Fe(CO)_5$ — a pentagonal bipyramid. However, the *equatorial* Cr–C bond distance is very long at the SCF level of treatment compared with the axial distance, whereas in $Fe(CO)_5$ the *axial* Fe–C distance is much longer than the equatorial distance (Luthi *et al.* [54]). This may be understood from the *d*-orbital occupations of the two species. In $Cr(CO)_5$, the occupation of the $^3A_2'$ state is predominantly $d_{xz}^2 d_{yz}^2 d_{x^2-y^2}^1 d_{xy}^1$, (see Hay [14], for example), giving the axial CO group (along z) a greater bonding interaction than the equatorial groups. In $Fe(CO)_5$, the configuration is $d_{xz}^2 d_{yz}^2 d_{x^2-y^2}^2 d_{xy}^2$, with only an empty d_{z^2} orbital, and in this case the equatorial groups are favoured over the axial groups. However, when extensive electron correlation is included, we expect the equatorial Cr–C distance would be significantly shortened, as found for the axial Fe–C distance in $Fe(CO)_5$. The C–O bond distances reflect the different Cr–C distances also — at the SCF level of theory the axial CO has a much stronger interaction with the Cr atom and so has a longer C–O bond distance. The equatorial CO has a weaker interaction and so a shorter C–O bond distance.

We now consider the C_{4v} structure, from the results in Table 4. At the SCF level of theory, the equatorial Cr–C distance is very similar to that in $Cr(CO)_6$, whereas the axial distance is slightly shorter, as may be expected with the removal of the opposing "axial" CO in $Cr(CO)_6$. The angle $\angle C_{ax}CrC_{eq}$ is in good agreement with the experimental estimate of 93°, and the 92° value of Demuynck *et al.* [16]. We note that there are also semi-empirical estimates of 93° [55] and 93.5° [56] for this angle. The angle $\angle CrC_{eq}O_{eq}$ is very close to 180°, as may be expected, and the C–O bond distances are both close to the C–O distance in $Cr(CO)_6$. Thus at the SCF level of theory, $Cr(CO)_5$ is only slightly perturbed from the $Cr(CO)_6$ structure. Given this fact, at the correlated level of theory we fix the C–O distances based on the $Cr(CO)_6$ correlated results. For the CCSD/CCSD(T) calculations we use a compromise distance which should be suitable for both methods. As noted previously, the angles are fixed at the SCF values.

At the MCPF level of theory, both Cr–C bond distances are fully optimized. In this case the axial bond distance contracts more than found in $Cr(CO)_6$ (see Table 2) and the equatorial distance a little less than in $Cr(CO)_6$. At the CCSD and CCSD(T) levels of theory, the axial bond contracts even further, which may be expected based on the $Cr(CO)_6$ results of Table 2. (Note that in this case we did not optimize the equatorial bond distance, fixing it at about the $Cr(CO)_6$ value). The additional contraction of the axial bond distance at the correlated level of theory is a consequence of configurational mixing of a low-lying $3d4p$ hybrid orbital in $Cr(CO)_5$, which is much higher lying in $Cr(CO)_6$, so that $Cr(CO)_5$ is more poorly described at the SCF level than $Cr(CO)_6$. This may be seen in the $\mathcal{T}_1$ diagnostic [57] from the coupled-cluster calculations, for example, which is around 0.032 in $Cr(CO)_6$ and around 0.038 in $Cr(CO)_5$.

A full optimization of both the Cr–C and C–O distances of $Cr(CO)_5$ at the CCSD(T) level in a larger basis is probably desirable — however, given the paucity of experimental data on the structure of $Cr(CO)_5$, this is postponed to a later date. An estimate of the optimal geometry was made by combining the $Cr(CO)_6$ and $Cr(CO)_5$ results presented here, and is given in the footnotes to Table 8.

3.4 Energetics

3.4.1 Basis set superposition error

In the previous work, we did not compute the BSSE associated with the total binding energy of $Cr(CO)_6$, although in earlier work on NiCO [58], $Ni(CO)_2$ [7] and TiCO [24], it was found that the BSSE and basis set expansion effects tended to cancel to a large extent. However, the recent work of Blomberg *et al.* [9] on $Ni(CO)_4$ indicated a large superposition error in a basis set larger than the small basis used here. Therefore we have considered the BSSE question in some detail. We note that Blomberg *et al.* found that the CCSD/CCSD(T) and MCPF methods gave similar results for the BSSE correction in $Ni(CO)_4$ (around 8% larger for the CCSD(T) method compared to MCPF), so that in the current work we use only the MCPF approach for the computation of the BSSE, using the full counterpoise method [59]. The results are given in Tables 5 and 6, where we break down the various contributions for the different systems and basis sets.

For the total binding energy of $Cr(CO)_6$ there is a large superposition error in the small basis, as shown in entry (1) of Table 5. At the correlated level of theory, the superposition error is around three times the SCF result (this seems to roughly hold for all the results presented in Table 5). The dominant contribution is from CO, with about 4 kcal/mol/CO, with a comparatively small contribution from the Cr atom. The overall BSSE correction of 28 kcal/mol is a very large correction to a total computed binding energy of about 110 kcal/mol — thus, even though this correction is an upper bound to the true correction, larger basis sets are essential in order to compute reliable energetic quantities.

In the large basis for $Cr(CO)_6$ (entry (2)) the superposition error is about half that of the small basis, at both the SCF and MCPF levels of theory. The SCF result is very good, slightly lower than the recent value of 7 kcal/mol given by Kunze and Davidson [13], even though the total energy of $Cr(CO)_6$ is about 0.01 E_h higher than their value. At the MCPF level of theory, the CO contribution to the superposition error is reduced to about 2 kcal/mol/CO, and the Cr contribution is reduced from the small basis result. The overall correction, although much improved from the small basis, is still large.

Using the large $3s3p$ basis (entries (3) and (4)), we see an overall *increase* in superposition error at both the SCF and MCPF levels of theory, when compared with entry (2), which has the same basis on CO but a smaller basis on Cr. We see that the Cr portion of the superposition error is reduced to almost nothing at the SCF level, and is significantly reduced at the correlated level. However, a side effect of using a large, flexibly contracted basis set on Cr is to increase the superposition error for the $(CO)_6$ fragment significantly — the SCF superposition error has increased by nearly 3 kcal/mol and the MCPF superposition error has increased by around 8 kcal/mol, when compared with the results in entry (2). These results indicate that even at the SCF level we need a larger basis — probably an additional contracted d function on each C and O. At the correlated level, the superposition error is again increased by almost three times the increase at the SCF level of theory. Thus, to reduce the superposition error significantly at the correlated level, the [4s 3p 2d 1f] ANO basis should be used on CO and would probably give very good results when combined with a larger Cr basis. However, as noted previously, this leads about 440 basis functions which is too large at the current time.

For the first bond dissociation energy of $Cr(CO)_5$ (equation (1)) the superposition error may be computed in two ways — indirectly as the difference between the superposition errors for the total binding energy of $Cr(CO)_6$ and the total binding energy of $Cr(CO)_5$, or directly using the appropriate fragments for equation (1).

From entry (1) in Table 6, we see that the BSSE for the total CO bond dissociation energy of $Cr(CO)_5$ is qualitatively similar to that for $Cr(CO)_6$ (entry (1) of Table 5), being roughly proportional to the number of CO ligands. For the first bond dissociation energy, we subtract the $Cr(CO)_6$ and $Cr(CO)_5$ numbers (entry (1) in Tables 5 and 6, respectively) giving a superposition error of 1.7 kcal/mol at the SCF level and 5.6 kcal/mol at the MCPF level. Alternatively, entry (2) of Table 6 gives the superposition error computed directly from fragments derived from equation (1). We see a much larger correction in this case, at both the SCF and MCPF levels of theory. The difference between the two corrections serves to illustrate the uncertainty in the estimation of BSSE via the counterpoise method.

In the large basis, we have only computed the BSSE via the indirect method. Entry (3) in Table 6 gives the results for the total binding energy of $Cr(CO)_5$. When compared with entry (1), the reduction in BSSE is similar to $Cr(CO)_6$ (entries (1) and (2) of Table 5). From these results, the BSSE for the first bond dissociation energy in the large basis is 0.7 kcal/mol at the SCF level and 2.3 kcal/mol at the MCPF level of treatment.

3.4.2 The total CO binding energy of $Cr(CO)_6$ and $Cr(CO)_5$

The total binding energies for $Cr(CO)_6$ and $Cr(CO)_5$ are given in Tables 7 and 8. We give both the total binding energy and the binding energy per CO molecule, with and without the correction for BSSE. In the small basis, we see that the CCSD method yields a binding energy which is slightly smaller than MCPF. The contribution from connected triple excitations (T) is very large, about 36 kcal/mol in $Cr(CO)_6$ compared with 30 kcal/mol in $Ni(CO)_4$ [9]. Thus the contribution per CO is about 1.5 kcal/mol smaller in $Cr(CO)_6$ than in $Ni(CO)_4$. In $Cr(CO)_5$ the triples contribution is about 31.5 kcal/mol and so the contribution per CO is slightly larger than in $Cr(CO)_6$ but smaller than $Ni(CO)_4$. After correcting for BSSE, the total binding energy is reduced significantly, as expected.

In the large basis at the MCPF level of theory, the total binding energy of $Cr(CO)_6$ is *reduced* by almost 10 kcal/mol compared to the small basis, which is undoubtedly due to the large reduction in BSSE. An analogous, though smaller, effect was found for NiCO [9] and NiN_2 [58]. However, after correction for BSSE, the large basis result is about 3 kcal/mol *larger* than the small basis result. In fact, the small and large basis results are remarkably close after correction for superposition error, indicating that the correction is probably meaningful, although still an upper bound.

In the large $3s3p$ basis set, we have computed the total binding energy including both $3s3p$ and valence correlation, and only the valence correlation. The effect of using a larger Cr basis is 6.1 kcal/mol at the valence level, whereas the effect of $3s3p$ correlation is only 3.8 kcal/mol, after correction for BSSE. Thus the total binding energy is increased by around 10 kcal/mol using the large $3s3p$ basis set and including $3s3p$ correlation. We note that relativistic effects, which we have not included here, are expected to contribute less than 5 kcal/mol to the total binding energy of $Cr(CO)_6$ [4, 9].

From the MCPF results in the large $3s3p$ basis set, and the CCSD(T) results in the small basis set, we estimate a CCSD(T) value of about 125 kcal/mol in the large $3s3p$ basis, including the effect of $3s3p$ correlation. This is around 77% of the experimental value, and is probably a lower bound, as calculations on NiCO [9] indicated that the CCSD(T) method may yield a greater increase in binding energy than MCPF on improving the basis set. This percentage is less than in $Ni(CO)_4$, for which the theoretical value is around 89% of the experimental value in a basis of similar size to our large basis, at the CCSD(T) level of theory. As discussed in § 1, for NiCO the use of a very large basis gave an additional 3.5 kcal/mol of binding energy compared to a smaller basis set, at the CCSD(T) level of theory. Recalling the large BSSE correction to the binding energy in our largest basis set, this indicates that the remaining discrepancy for $Cr(CO)_6$ is probably due to one-particle basis set limitations, and the use of a basis such as the [4*s* 3*p* 2*d* 1*f*] ANO set for CO with the CCSD(T) method would give very good results.

For the total binding energy of $Cr(CO)_5$ (Table 8) we obtain results similar to $Cr(CO)_6$ on going from MCPF to CCSD(T), although the total increase in binding energy is lower. The binding energy per CO molecule is seen to be about 3-4 kcal/mol larger for $Cr(CO)_6$ than $Cr(CO)_5$. Again in the large basis set the binding energy is reduced significantly compared to the small basis set result, but is slightly larger after inclusion of the BSSE correction. We note that the geometry was not optimized for the large basis calculation but was taken from a combination of the small basis set results and the results for $Cr(CO)_6$. However, a full optimization of the geometry would probably only lead to a small correction to the total binding energy. For example, in $Cr(CO)_6$ a Cr–C bond distance which is inaccurate by 0.03 a_0 gives a total energy which is 0.5 kcal/mol higher than the minimum energy, and a C–O bond distance which is in error by 0.03 a_0 gives a total energy which is less than 2 kcal/mol higher. Based on this, we expect that a full optimization of the $Cr(CO)_5$ structure would yield less than 2 kcal/mol additional binding energy. We note that there is no direct experimental determination of the total binding energy of $Cr(CO)_5$.

3.4.3 The first CO bond dissociation energy of $Cr(CO)_6$

The results for the first CO bond dissociation energy are given in Table 9. There are two recent experimental determinations, both of which agree on the value of 37 kcal/mol at 298 K [60, 61]. We have corrected these to a D_e value at 0 K by using harmonic vibrational frequencies computed at the SCF level of theory in the small basis for $Cr(CO)_6$ and $Cr(CO)_5$ and a standard correction [62] for translational and rotational degrees of freedom ($\frac{7}{2}$RT for equation (1)). Although the SCF method does not describe the structure and force constants of these molecules particularly well, the vibrational correction based on these frequencies is remarkably good. For example, for equation (2) the total correction due to zero-point and vibrational-excitation is 19.7 kcal/mol computed using the experimental frequencies for $Cr(CO)_6$ [28, 63] and CO [41], and 18.8 kcal/mol when computed using the SCF frequencies. This agreement is fortuitous, because there is a cancellation of errors between the $Cr(CO)_6$ and free CO calculations, and between the zero-point and vibrational-excitation corrections. The Cr–C stretch frequencies are too low at the SCF level, leading to increased vibrational-excitation at 298 K (0.5 kcal too high), whereas the C–O stretches are too high (in $Cr(CO)_6$), leading to a zero-point correction for equation (2) which is 1.4 kcal/mol too small, giving a net error of only 0.9 kcal/mol. The combined error of around 2 kcal/mol is still remarkably small, however, and since we may expect similar results for $Cr(CO)_5$, the correction for equation (1) of 1.6 kcal/mol should be reliable.

For the first bond dissociation energy, the results in the small basis set are already in good agreement with experiment. The CCSD(T) value is almost 8 kcal/mol larger than MCPF, and interestingly the CCSD value is superior to the MCPF value. We recall from § 3.2 that the CCSD method also gave Cr–C bond distances and force constants which were superior to the MCPF values. Thus it seems that the CCSD method, which is not as good as MCPF for free CO or the total binding energies of $Cr(CO)_6$ and $Cr(CO)_5$, describes the Cr–CO interaction more accurately in these systems, and also yields a more balanced description of $Cr(CO)_6$ and $Cr(CO)_5$. This is similar to results found for NiCO and $Ni(CO)_2$ previously [9].

After correcting for superposition error (using the indirect method — see § 3.4.1) we see that the CCSD(T) method yields a very good value for the first bond dissociation energy. In the large basis the MCPF approach yields about a 1 kcal/mol increase in the first bond dissociation energy (after correction for BSSE). There are several sources of uncertainty in the first bond dissociation energy. The $Cr(CO)_5$ structure was not fully optimized in either basis set, which may reduce the first bond dissociation energy by 1-2 kcal/mol (by increasing the total binding energy of $Cr(CO)_5$ — see § 3.4.2). The BSSE correction is somewhat uncertain, as discussed earlier, and the true computed binding energy may be smaller, as indicated by the figures in brackets in Table 9. We note, however, that the BSSE correction is relatively small in the large basis, and the MCPF approach yields a very similar first bond dissociation energy in both basis sets, so that this error is probably fairly small. We note that test calculations indicate that differential $3s3p$ correlation effects between $Cr(CO)_6$ and $Cr(CO)_5$ are less than 1 kcal/mol. Overall, these uncertainties are small, and an estimated value of around 38 kcal/mol for the first bond dissociation energy for the CCSD(T) method in the large basis set is not unreasonable and is in very good agreement with the experimental value.

4 Conclusions

The geometric structures and energetics of $Cr(CO)_6$ and $Cr(CO)_5$ were determined at the MCPF, CCSD and CCSD(T) levels of theory. For $Cr(CO)_6$, the structure and force constants for the totally symmetric representation are in good agreement with experimental data once basis set limitations are taken into account. A basis set study of free CO is used to illustrate these limitations, and it is found that in the largest basis sets the CCSD(T) method gives excellent agreement with experiment for the bond length, dipole moment and harmonic frequency of free CO. The total binding energy of $Cr(CO)_6$ is estimated to be around 125 kcal/mol in our largest basis set at the CCSD(T) level of theory, or about 77% of the experimental value, after accounting for superposition error. The effect of $3s3p$ correlation is found to be small. The remaining discrepancy between the experimental and theoretical total binding energy of $Cr(CO)_6$ is probably due to limitations in the one-particle basis, rather than limitations in the correlation treatment, and an additional d function and an f function on each C and O are needed to obtain quantitative results. This is underscored by the fact that even using a very large primitive set (1042 primitive functions contracted to 300 basis functions), the superposition error for the total binding energy of $Cr(CO)_6$ is 22 kcal/mol at the MCPF level of treatment. In contrast, the first bond dissociation energy of $Cr(CO)_6$ is very well described at the CCSD(T) level of theory, due to a cancellation of basis set incompleteness errors for $Cr(CO)_6$ and $Cr(CO)_5$, and our best estimated value of 38 kcal/mol is within the experimental error bars.

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Table 1: Summary of the free CO results

	r_e a_0[c]	μ_{ff}[a] a.u.[d]	μ_{ex}[b] a.u.[d]	k aJ/Å^2 [e]	ω_e cm^{-1}
CO [4*s* 3*p*] segmented					
SCF	2.12401	−0.20405	−0.20405	20.7856	2268.4
MCPF	2.18676	−0.06333	0.04979	15.9810	1989.0
CCSD	2.18029	−0.05904	–	16.6810	2032.1
CCSD(T)	2.19548	−0.05466	–	15.4724	1957.1
CO [4*s* 3*p* 1*d*] ANO					
MCPF	2.15006	0.03483	0.11670	18.7736	2155.7
CCSD	2.14399	0.03081	–	19.4655	2195.2
CCSD(T)	2.15717	0.04667	–	18.2464	2125.3
CO [4*s* 3*p* 2*d* 1*f*] ANO					
MCPF	2.13906	0.03054	0.10804	19.2053	2180.4
CCSD	2.13341	0.02626	–	19.8441	2216.4
CCSD(T)	2.14684	0.04226	–	18.6058	2146.1
CO [5*s* 4*p* 3*d* 2*f* 1*g*] ANO					
MCPF	2.13094	0.03083	0.10516	19.4227	2192.7
CCSD	2.12557	0.02692	–	20.0331	2226.9
CCSD(T)	2.13913	0.04096	–	18.7766	2156.0
CO [5 + 1*s* 4 + 1*p* 3 + 1*d* 2 + 1*f* 1 + 1*g*] ANO					
MCPF	2.12933	0.03251	0.10620	19.5506	2200.0
CCSD	2.12402	0.02868	–	20.1580	2233.9
CCSD(T)	2.13754	0.04244	–	18.8932	2162.6

Table 1: cont. Summary of the free CO results

	r_e a_0[c]	μ_{ff}[a] a.u.[d]	μ_{ex}[b] a.u.[d]	k aJ/Å^2 [e]	ω_e cm^{-1}
CO [6*s* 5*p* 4*d* 3*f* 2*g*] ANO					
MCPF	2.12879	0.03234	0.10581	19.5653	2200.8
CCSD	2.12350	0.02849	–	20.1652	2234.3
CCSD(T)	2.13702	0.04224	–	18.8981	2162.9
CO [6*s* 5*p* 4*d* 3*f* 2*g* 1*h*] ANO					
MCPF	2.12863	0.03207	0.10544	19.6043	2203.0
MCPF+REL	2.12839	0.03257	–	19.5808	2201.7
CCSD	2.12336	0.02823	–	20.2065	2236.5
CCSD(T)	2.13688	0.04199	–	18.9387	2165.2
CO [6*s* 5*p* 4*d* 3*f* 2*g* 1*h*] ANO + (1*s* 1*p* 1*d*)					
MCPF	2.12860	0.03325	0.10654	19.6014	2202.8
MCPF+REL	2.12836	0.03388	–	19.5777	2201.5
CCSD	2.12333	0.02940	–	20.2047	2236.4
CCSD(T)	2.13684	0.04321	–	18.9349	2165.0
CO Scuseria [10*s* 9*p* 4*d* 2*f* 1*g*]					
CCSD	2.1316[f]	0.026	–	–	–
CCSD(T)	2.1316[f]	0.049	–	–	–
Experiment	2.1322[g]	0.0481[h]	0.0481[g]	19.0186	2169.8[g]

[a] Computed using a finite field (energy derivative) approach (see § 2)

[b] Computed as an expectation value

[c] 1 a_0 = 0.529177 Å

[d] 1 a.u. = 2.541748 D. A positive dipole moment indicates polarity C^-O^+

[e] 1 aJ/Å^2 = 1 mdyne/Å

[f] Not optimized

[g] Huber and Herzberg [41]

[h] Equilibrium value [42]

Table 2: Bond lengths for $Cr(CO)_6$, valence only (a_0)

	r(Cr–C)	r(C–O)
Small basis		
SCF	3.775	2.142
MCPF	3.692	2.215
CCSD	3.684	2.207
CCSD(T)	3.664	2.227
Large basis		
MCPF	3.666	2.165
Expt[a]	3.616	2.154

[a] Bond distances are from Jost *et al.* [51]. See also Rees and Mitschler [52].

Table 3: Force constants for $Cr(CO)_6$, valence only ($aJ/Å^2$)[a]

	F_{11}	F_{22}	F_{12}
Small basis			
MCPF	15.18	2.06	0.31
CCSD	15.70	2.21	0.31
CCSD(T)	14.44	2.24	0.27
Large basis			
MCPF	18.75	2.32	0.23
Expt[b]	18.11	2.44	0.38
Expt Error	±0.16	±0.02	±0.13

[a] In the notation of Jones *et al.* [28]. F_{11} is for the totally symmetric C–O stretch, F_{22} is for the totally symmetric Cr–C stretch and F_{12} is the coupling term.

[b] Jones *et al.* [28].

Table 4: $Cr(CO)_5$ bond distances and angles, valence only (a_0 and degrees)

	$r(\text{Cr–C})_{ax}$	$r(\text{C–O})_{ax}$	$r(\text{Cr–C})_{eq}$	$r(\text{C–O})_{eq}$	$\angle \text{C}_{ax}\text{CrC}_{eq}$	$\angle \text{CrC}_{eq}\text{O}_{eq}$
$^1A_1$ C_{4v}						
SCF	3.734	2.144	3.772	2.146	92.5	179.4
MCPF	3.624	2.215[a]	3.708	2.215[a]	92.5[a]	179.4[a]
CCSD	3.567	2.220[a]	3.670[a]	2.220[a]	92.5[a]	179.4[a]
CCSD(T)	3.554	2.220[a]	3.670[a]	2.220[a]	92.5[a]	179.4[a]
$^3A_2'$ D_{3h}						
SCF	3.737	2.153	3.927	2.135		

[a] Not optimized (see text)

Table 5: Basis set superposition errors for various $Cr(CO)_6$ fragments (kcal/mol)

	SCF	MCPF
(1) Small basis, valence only		
Cr + $(CO)_6$ (ghost)	0.6	3.1
$(CO)_6$ + Cr (ghost)	8.6	24.5
Sum	9.2	27.6
(2) Large basis, valence only		
Cr + $(CO)_6$ (ghost)	0.6	2.5
$(CO)_6$ + Cr (ghost)	4.7	12.9
Sum	5.3	15.4
(3) Large $3s3p$ basis, valence only		
Cr + $(CO)_6$ (ghost)	0.0	0.8
$(CO)_6$ + Cr (ghost)	8.0	21.1
Sum	8.0	21.9
(4) Large $3s3p$ basis, $3s3p$ + valence		
Cr + $(CO)_6$ (ghost)	0.0	1.5
$(CO)_6$ + Cr (ghost)	8.0	21.1
Sum	8.0	22.6

Table 6: Basis set superposition errors for various $Cr(CO)_5$ fragments, valence only (kcal/mol)

	SCF	MCPF
(1) Small basis		
Cr + $(CO)_5$ (ghost)	0.5	2.8
$(CO)_5$ + Cr (ghost)	7.1	19.2
Sum	7.6	22.0
(2) Small basis		
$Cr(CO)_5$ + CO (ghost)	1.8	4.4
CO + $Cr(CO)_5$ (ghost)	2.8	6.0
Sum	4.6	10.4
(3) Large basis		
Cr + $(CO)_5$ (ghost)	0.5	2.3
$(CO)_5$ + Cr (ghost)	4.1	10.8
Sum	4.6	13.1

Table 7: Total CO binding energies for $Cr(CO)_6$ (kcal/mol)

	BE	BE/N_{CO}	BE-BSSE	(BE-BSSE)/N_{CO}
Small basis, valence only				
MCPF	109.5	18.3	81.9	13.6
CCSD	103.3	17.2	75.7	12.6
CCSD(T)	139.4	23.2	111.8	18.6
Large basis, valence only				
MCPF	100.0	16.7	84.6	14.1
Large 3*s*3*p* basis, valence only[c,d]				
MCPF	112.5	18.8	90.7	15.1
Large 3*s*3*p* basis, 3*s*3*p* + valence[c,e]				
MCPF	117.1	19.5	94.5	15.8
Expt	162[a]	27	162	27

[a] The experimental binding energy corresponding to D_0^{298} is 153 kcal/mol, from Pittam *et al.* [64]. The value given here corresponds to D_e, derived using the data summarized by Pilcher *et al.* [63].

[b] At the small basis geometry

[c] At the large basis geometry. The total energy is –1719.92269 a.u. at the SCF level of theory.

[d] The MCPF method, using 4,223,071 configurations, yields a total energy of –1722.30217 a.u.

[e] The MCPF method, using 5,321,953 configurations, yields a total energy of –1722.64952 a.u.

Table 8: Total CO binding energies for $Cr(CO)_5$, valence only (kcal/mol)

	BE	BE/N_{CO}	BE-BSSE	(BE-BSSE)/N_{CO}
Small basis				
MCPF	74.8	15.0	52.8	10.6
CCSD	65.1	13.0	43.1	8.6
CCSD(T)	96.7	19.3	74.7	15.0
Large basis[a]				
MCPF	67.8	13.6	54.7	10.9

[a] Geometry not optimized (see text). $r(\mathrm{Cr–C})_{ax}$=3.600 a_0, $r(\mathrm{Cr–C})_{eq}$=3.680 a_0, and $r(\mathrm{C–O})_{ax}=r(\mathrm{C–O})_{eq}$=2.165 a_0

Table 9: First CO binding energy of $Cr(CO)_6$, valence only (kcal/mol)

$Cr(CO)_6 \rightarrow Cr(CO)_5 + CO$		
	ΔE	ΔE-BSSE[a]([b])
Small basis		
MCPF	34.8	29.1 (24.3)
CCSD	38.8	32.6 (27.8)
CCSD(T)	42.7	37.1 (32.3)
Large basis		
MCPF	32.3	30.0
Experimental data		
D_0^{298}	37	37
D_e	38.6[c]	38.6
Expt Error	±5[d],±2[e]	±5,±2

[a] Corrected using the indirectly computed BSSE values (see text)

[b] Corrected using the directly computed BSSE values (see text)

[c] Correction of 1.6 kcal/mol based on theoretical results (see text)

[d] Bernstein *et al.* [60].

[e] Lewis *et al.* [61].