

Regular article

Calculation of accurate binding energies for the transition-metal carbonyls Ni(CO)₄, Fe(CO)₅ and Cr(CO)₆

B. Joakim Persson, Peter R. Taylor

Department of Chemistry and Biochemistry and San Diego Supercomputer Center, MC0505,
University of California, San Diego, La Jolla, CA 92093-0505, USA

Received: 7 May 2002 / Accepted: 20 November 2002 / Published online: 6 October 2003
© Springer-Verlag 2003

Abstract. Using new atomic natural orbital basis sets constructed to treat correlation of all *M*-shell electrons for the first transition row, we have calculated the energies of the reaction $M(\text{CO})_n \rightarrow M + n\text{CO}$ for $M = \text{Ni}, \text{Fe}, \text{Cr}$ and $n = 4, 5, 6$, respectively. Both coupled-cluster and multiconfigurational reference perturbation theory are used as correlation treatments, and although they give qualitatively similar results once basis set superposition error is accounted for, multireference perturbation theory gives binding energies that are larger than both coupled-cluster theory and experiment. The agreement between our best calculated results and experiment is excellent for Ni(CO)₄ and Fe(CO)₅, but very poor for Cr(CO)₆. The experimental result for the latter is old and we suggest that revisiting this system experimentally would be valuable.

titative accuracy in agreement with experiment was that on Ni(CO)₄ by Blomberg et al. [2], who used the coupled-cluster method with single and double substitutions and a perturbational treatment of triple substitutions [CCSD(T)] method and basis sets of valence double-zeta plus polarization quality. Their CCSD(T) binding energy was some 13 kcal/mol smaller than the experimental estimate, an enormous improvement on their modified coupled-pair functional result, which was 30 kcal/mol too small. Similar success was achieved for Fe(CO)₅ and Cr(CO)₆ by Barnes and co-workers [3, 4], although the calculated binding energies were up to 40 kcal/mol too small. However, a rather different picture was obtained by Persson et al. [1], using multiconfigurational reference perturbation theory (specifically, complete-active-space second order perturbations theory CASPT2 [5]) with a large atomic natural orbital (ANO) basis. Agreement between experiment and CASPT2 was initially rather poor, but once a (substantial) counterpoise correction [6] for basis set superposition error (BSSE) was applied, agreement between CASPT2 and experiment improved dramatically. Of course, this implies that correcting for BSSE in the coupled-cluster calculations of Refs. [2, 3, 4] would then significantly worsen the agreement between CCSD(T) and experiment. This issue has remained unresolved.

1 Introduction

There have been numerous theoretical investigations of the transition-metal carbonyls and these are discussed extensively in Ref. [1]. Work cited there includes calculations of structure and binding energies (total and successive CO binding), and the interested reader is referred there for a complete discussion. Here we focus on the energy required to dissociate the closed-shell carbonyls Ni(CO)₄, Fe(CO)₅, and Cr(CO)₆ to a metal atom and free CO molecules. Experimental values are available for all three molecules and these have often been used to gauge the reliability of different many-electron treatments. The earliest study to achieve quan-

A key question in calculations on transition-metal compounds is the importance of correlating the metal 3*s* and 3*p* electrons. Doing this substantially increases the cost of most orbital-based calculations (i.e., we do not discuss density functional theory methods here), but it appears essential if high accuracy is to be achieved. Given that correlating the entire *M* shell is necessary, the next question is what this implies for the transition-metal basis sets used. First, most of the available sets emphasize flexibility in the “valence” region (defined here as 3*d*, 4*s*, and perhaps 4*p*) and contract as many functions as possible to keep the basis set small in the “core” region, which invariably includes 3*s* and 3*p*. Radial correlation of the latter is likely to require *s* and *p* functions that are not present in the contracted basis. Angular correlation may be somewhat better described – one might hope that

Contribution to the Björn Roos Honorary Issue

Correspondence to: P. R. Taylor
e-mail: P.R.Taylor@warwick.ac.uk

Present address: P. R. Taylor, Department of Chemistry,
University of Warwick, Coventry CV4 7AL, UK

a flexible valence basis would contain enough d shells to describe angular correlation, but even so higher d exponents may be required, and typically no higher angular functions appropriate to $3s3p$ correlation would be included. It is clearly somewhat dangerous to try to draw conclusions about correlation of these “core” electrons using basis sets constructed and optimized for valence correlation, just as is the case when treating core correlation in first-row and second-row elements.

Recently, one of us (B.J.P., unpublished) has constructed new ANO basis sets for the first transition row. These sets incorporate $3s3p$ correlation from the outset and thus should be more effective for molecular calculations in which these electrons are correlated, and extensive testing on molecules during construction of these sets supports this thesis. These new ANO sets provide an ideal means of reinvestigating the binding energies of the transition-metal carbonyls, especially because we expect well-designed ANO basis sets to have relatively small BSSEs. In this work we show that these new basis sets provide calculated binding energies that agree well with experiment, at least for $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$, and do indeed lead to small BSSE corrections. We speculate that the discrepancy between our best computed value and experiment for $\text{Cr}(\text{CO})_6$ arises from some error in the experimental determination.

2 Computational methods

All CCSD(T) results presented here were obtained with the program Molpro2000 [7]; all CASPT2 results were obtained with the program system MOLCAS [8]. In general, calculations were run both with and without correlation of the metal $3s3p$ electrons, using the same basis sets in each case. The $1s$ electrons on the ligands and the $1s2s2p$ electrons on the metal were not correlated in any calculations. The transition-metal basis sets are the new ANO sets from Persson discussed earlier, based on a (21s 14p 8d 6f 4g) primitive set contracted to [8s 7p 6d 5f 4g], [7s 6p 5d 4f 3g] or [6s 5p 4d 3f 2g]. We include some calculations with the smallest contraction, [5s 4p 3d 2f 1g], which performs quite well here, but our experience in other calculations is that this basis is too small to perform acceptably in molecular calculations. The C and O basis sets are [4s 3p 2d 1f] ANO sets [9].

Geometries were taken from Ref. [1] and have point-group symmetry T_d , D_{3h} and O_h for $\text{Ni}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$, respectively. Binding energies were computed by dissociating each molecule to ground-state CO molecules and metal atoms in their ground electronic states, Ni ($d^9s^1\ ^3D$), Fe ($d^6s^2\ ^5D$) and Cr ($d^5s^1\ ^7S$). Since the CCSD(T) method is size-extensive, we simply computed the energies of the fragments from separate calculations. For the CASPT2 calculations, the active space chosen [1] localizes completely on the metal as the $M-C$ bonds are stretched, and thus at infinite separation the CASPT2 calculation on the ligands reduces to a second-order Møller–Plesset (MP2) calculation. We originally estimated the total energy at dissociation from MP2 calculations on the ligands and CASPT2 calculation on the metal, but this created some difficulties when level-shifting [8] was employed in CASPT2 calculations on the complexes, and we replaced the MP2 results with CASPT2 results. This is a subtle but significant issue, since in the absence of level-shifting the two approaches will of course give the same answer, and we return to it briefly at the end of this section. All total energies are corrected for relativistic effects using first-order perturbation theory at the self-consistent-field (SCF) level for the CCSD(T) calculations and at the CASSCF level for the CASPT2 calculations.

BSSE was corrected for using a counterpoise correction. For the metal-atom BSSE, the ghost basis used was that of the ligands. The

issue of what electronic state to use for the metal atom is something of a vexed question. Following Ref. [1] we chose a singlet state with occupation d^{n+2} for each case, since this seems most appropriate to the bonding in the complex. We may note that since this atomic state is more difficult to describe (larger correlation effects) than any sensible choice arising from $d^n s^2$ or $d^{n+1} s$, our choice is likely to exaggerate the effect of BSSE somewhat rather than underestimating it. For the ligand BSSE, we removed the metal atom and electrons, leaving the metal basis in the centre of the system. The ligand BSSE correction is thus that from the metal basis only, not the basis set on other ligands.

Zero-point vibrational corrections to the binding energy were estimated from experimental frequencies, as was done in Ref. [1].

As a final methodological issue, as we noted earlier some care is needed when level-shifting is employed to improve the convergence of CASPT2 calculations. In particular, for convenience we originally calculated the energy of the $n\text{CO}$ dissociation fragment using a closed-shell MP2 scheme. This is completely consistent with the choice of active space used in the CASSCF calculations: there are no active orbitals on the ligands at dissociation. Consequently, if we use the MOLCAS CASPT2 program to calculate the energy of the $n\text{CO}$ molecules with an empty active space we expect to recover the same result as with MP2. Unfortunately, this equivalence is obtained only when no level shift is used in the CASPT2 program. Although the procedure used for real energy shifts [8] attempts to correct for effects of the shift on the total energy, this is not completely effective, and the total energy tends to increase somewhat with the shift used. Unless all calculations used in the binding energy calculations use the same shift, a significant error (e.g., 10 kcal/mol) can be seen in the computed binding energy. We may note in passing that with the use of an imaginary level shift, as advocated by Forsberg and Malmqvist [10], the total energies appear unaffected by the shift, and we saw no inconsistencies in the calculated binding energies.

3 Results and discussion

3.1 $\text{Ni}(\text{CO})_4$

CCSD(T) total energies relevant to the binding energy of $\text{Ni}(\text{CO})_4$ are listed in Table 1. We also include results obtained with the smallest Ni ANO set, [5s 4p 3d 2f 1g]. The valence-correlated results with this basis are fair, but inclusion of $3s3p$ correlation leads to very large superposition errors on the metal atom. Experience in other calculations suggests that this smallest ANO set is too small for reliable use in molecules. As expected, the BSSE on Ni decreases substantially as the basis set is extended, and even with core–valence correlation included is less than 2 kcal/mol in the largest [8s 7p 6d 5f 4g] ANO set. However, the BSSE on the CO ligands increases as the basis is extended, and thus the total BSSE, metal plus ligands, does not behave monotonically as the metal basis set is extended, at least when core–valence correlation is not included. All BSSE corrections are large and suggest that the combination of at least the larger ANO Ni sets with the ligand atom [4s 3p 2d 1f] sets is not well balanced. Increasing the ligand atom sets to, say, [5s 4p 3d 2f] or [5s 4p 3d 2f 1g] is hardly feasible, and for angular momentum balance would probably then require inclusion of h functions in the metal basis set.

Despite the nonmonotonic behaviour of the BSSE with metal basis set size, the binding energy after the BSSE correction increases steadily as the metal basis is improved. We note that the improvement in the binding

Table 1. Ni(CO)₄ coupled-cluster method with single and double substitutions and a perturbational treatment of triple substitutions [CCSD(T)] results (total energies in E_h , energy differences in kilocalories per mole)

	Ni basis set (<i>cc</i> -pVTZ on C and O)			
	[5s 4p 3d 2f 1g]	[6s 5p 4d 3f 2g]	[7s 6p 5d 4f 3g]	[8s 7p 6d 5f 4g]
Ni(CO) ₄	-1960.047712	-1960.073455	-1960.084739	-1960.091252
+ CV	-1960.402003	-1960.478458	-1960.509892	-1960.523601
Ni(<i>d</i> ¹⁰)	-1507.143312	-1507.172831	-1507.180674	-1507.183262
+ CV	-1507.472287	-1507.570401	-1507.607316	-1507.620125
Ni(<i>d</i> ¹⁰)+ghost COs	-1507.157803	-1507.177097	-1507.182324	-1507.184149
+ CV	-1507.519490	-1507.589364	-1507.614302	-1507.623066
(CO) ₄	-452.608882	-452.608882	-452.608882	-452.608882
+ ghost Ni	-452.612989	-452.615142	-452.617763	-452.620603
Ni(<i>d</i> ^{9s})	-1507.201624	-1507.230203	-1507.239380	-1507.242141
+ CV	-1507.529068	-1507.626464	-1507.664542	-1507.677565
CO	-113.153719	-113.153719	-113.153719	-113.153719
4CO	-452.614876	-452.614876	-452.614876	-452.614876
BSSE on Ni	9.1	2.7	1.0	0.6
+ CV	29.6	11.9	4.4	1.8
BSSE on (CO) ₄	2.6	3.9	5.6	7.4
Total BSSE	11.7	6.6	6.6	8.0
+ CV	32.2	15.8	10.0	9.2
D_e to Ni(<i>d</i> ¹⁰)	183.9	181.5	183.7	186.2
+ CV	199.8	186.2	182.8	183.3
Ni(<i>d</i> ^{9s}) → Ni(<i>d</i> ¹⁰)	36.6	36.0	36.8	36.9
+ CV	35.6	35.2	35.9	36.0
D_e to Ni(<i>d</i> ^{9s})	145.1	143.3	144.6	147.0
+ CV	161.9	148.8	144.6	145.1
BSSE corrected	133.4	136.7	138.0	139.1
+ CV	129.7	133.0	134.7	135.9
Relativity added ^a	141.8	145.1	146.4	147.5
+ CV	138.1	141.4	143.1	144.3
D_0^b	135.4	138.4	139.7	140.8
+ CV	131.4	134.7	136.4	137.6
Expt. [11]				138 ± 1

^a Relativity correction +8.4 kcal/mol^b Zero-point correction -6.7 kcal/mol

energy going from [6s 5p 4d 3f 2g] to [7s 6p 5d 4f 3g] is larger than that from the latter to [8s 7p 6d 5f 4g] only when the BSSE-corrected results are used and where 3s3p correlation is excluded. If the uncorrected results are used the binding energy improvement behaves in the reverse fashion, which seems physically implausible. Further, when 3s3p correlation is included the binding energy without the BSSE correction does not even change monotonically as the basis set is improved. The explanation lies in the increased BSSE on the CO ligands, as described earlier.

The relativistic contribution to the binding energy is calculated to be 8.4 kcal/mol. After inclusion of zero-point corrections and relativistic effects, we can see from the table that the predicted binding energy is in almost perfect agreement with experiment, at least when 3s3p correlation is included. The surprising thing is that including the latter reduces the binding energy. This is very unusual. The normal expectation, based on many observations, is that including core–valence correlation tends to increase binding energies. We may note that it is not correcting for BSSE that is responsible for the apparent anomaly, because it is observed even before the counterpoise correction is applied. Nor is it related to correcting the dissociation asymptote, since it is observed for dissociation to both Ni(*d*¹⁰) and Ni(*d*^{9s}). It is

tempting to look at the basis set convergence in Table 1 and to conclude that further basis set extension would hardly increase the computed binding energy by more than 1 kcal/mol. Such a conclusion would be too hasty. We have investigated here only the convergence with respect to the transition-metal basis: we have little or no evidence as to what improving the ligand basis would do, other than that one expects it to increase the computed binding energy.

The CASPT2 results of Table 2 are not as encouraging as their coupled-cluster counterparts. The calculated binding energies are considerably larger than the CCSD(T) results, and even after correction for BSSE seem too large. While the use of a larger active space might ameliorate things, it seems difficult to avoid the conclusion that the CASPT2 method greatly exaggerates the strength of the binding here. It must surely be the case, for instance, that improvements in the basis set would only increase the computed binding energy further, making matters worse.

One significant feature of Table 2 is that the inclusion of core–valence correlation increases the calculated binding energy, which is consistent with naive expectations but as we noted is not what is observed for the CCSD(T) calculations. At first sight this seems to be a major discrepancy between the CCSD(T) and CASPT2

Table 2. Ni(CO)₄ complete-active-space second-order perturbation theory (CASPT2) results (total energies in E_h , energy differences in kilocalories per mole)

	Ni basis set (<i>cc</i> -pVTZ on C and O)			
	[5s 4p 3d 2f 1g]	[6s 5p 4d 3f 2g]	[7s 6p 5d 4f 3g]	[8s 7p 6d 5f 4g]
Ni(CO) ₄	-1959.961628	-1959.987158	-1959.998762	-1960.005457
+ CV	-1960.328041	-1960.403656	-1960.435379	-1960.449582
Ni(<i>d</i> ¹⁰)	-1507.130662	-1507.158712	-1507.167268	-1507.169889
+ CV	-1507.461213	-1507.556787	-1507.594318	-1507.607580
Ni(<i>d</i> ¹⁰) + COs	-1507.143684	-1507.163345	-1507.168971	-1507.170919
+ CV	-1507.507009	-1507.575963	-1507.601543	-1507.610816
CO	-113.129534	-113.129534	-113.129534	-113.129534
4CO	-452.518136	-452.518136	-452.518136	-452.518136
(CO) ₄	-452.526085	-452.526085	-452.526085	-452.526085
+ ghost Ni	-452.530693	-452.533031	-452.535845	-452.538896
Ni(<i>d</i> ^{9s})	-1507.193099	-1507.220171	-1507.229305	-1507.232043
+ CV	-1507.522061	-1507.616778	-1507.655001	-1507.668354
BSSE on Ni	8.2	2.9	1.1	0.6
+ CV	28.7	12.0	4.5	2.0
BSSE on (CO) ₄	2.9	4.4	6.1	8.0
Total BSSE	11.1	7.3	7.2	8.7
+ CV	31.6	16.4	10.7	10.1
D_e to Ni(<i>d</i> ^{9s})	157.1	156.2	157.7	160.2
+ CV	180.6	168.6	164.6	165.1
BSSE corrected	146.1	148.9	150.5	151.5
+ CV	149.0	152.2	153.9	155.0
Relativity corrected ^a	154.5	157.3	158.9	159.9
+ CV	157.4	160.6	162.3	163.4
D_0^b	147.8	150.6	152.2	153.2
+ CV	150.7	153.9	155.6	156.7
Expt. [11]				138 ± 1

^a Relativity correction +8.4 kcal/mol^b Zero-point correction -6.7 kcal/mol**Table 3.** Fe(CO)₅ CCSD(T) results (total energies in E_h , energy differences in kilocalories per mole)

	Fe basis set (<i>cc</i> -pVTZ on C and O)			
	[5s 4p 3d 2f 1g]	[6s 5p 4d 3f 2g]	[7s 6p 5d 4f 3g]	[8s 7p 6d 5f 4g]
Fe(CO) ₅	-1828.644159	-1828.663368	-1828.673505	-1828.681590
+ CV	-1829.013555	-1829.074479	-1829.099055	-1829.112424
Fe(<i>d</i> ⁸)	-1262.428962	-1262.446557	-1262.451651	-1262.453337
+ CV	-1262.756070	-1262.840056	-1262.870636	-1262.881580
Fe(<i>d</i> ⁸) + ghost COs	-1262.438707	-1262.450318	-1262.453305	-1262.454303
+ CV	-1262.807418	-1262.860931	-1262.878353	-1262.884465
(CO) ₅	-565.724708	-565.724708	-565.724708	-565.724708
+ ghost Fe	-565.730715	-565.734201	-565.738042	-565.742847
Fe(<i>d</i> ^{6s²})	-1262.643075	-1262.658921	-1262.664387	-1262.666208
+ CV	-1262.967374	-1263.048251	-1263.079075	-1263.090226
CO	-113.153719	-113.153719	-113.153719	-113.153719
5CO	-565.768595	-565.768595	-565.768595	-565.768595
BSSE on Fe	6.1	2.4	1.0	0.6
+ CV	32.2	13.1	4.8	1.8
BSSE on (CO) ₅	3.8	6.0	8.4	11.4
Total BSSE	9.9	8.3	9.4	12.0
+ CV	36.0	19.1	13.2	13.2
D_e to Fe(<i>d</i> ^{6s²})	145.9	148.0	150.9	154.9
+ CV	174.2	161.7	157.7	159.1
BSSE corrected	136.0	139.7	141.5	142.9
+ CV	138.2	142.6	144.5	145.9
Relativity corrected ^a	139.4	143.1	144.9	146.3
+ CV	141.6	146.0	147.9	149.3
D_0^b	129.0	132.7	134.5	135.9
+ CV	131.2	135.6	137.5	138.9
Expt. [12]				136.7

^a Relativity correction +3.4 kcal/mol^b Zero-point correction -10.4 kcal/mol

Table 4. Fe(CO)₅ CASPT2 results (total energies in E_h , energy differences in kilocalories per mole)

	Fe basis set (<i>cc</i> -pVTZ on C and O)			
	[5s 4p 3d 2f 1g]	[6s 5p 4d 3f 2g]	[7s 6p 5d 4f 3g]	[8s 7p 6d 5f 4g]
Fe(CO) ₅	-1828.558204	-1828.577927	-1828.588313	-1828.596631
+CV	-1828.935225	-1828.997975	-1829.023376	-1829.037386
Fe(<i>d</i> ⁸)	-1262.397699	-1262.416190	-1262.422410	-1262.424320
+CV	-1262.723589	-1262.807769	-1262.839497	-1262.851205
Fe(<i>d</i> ⁸) + ghost COs	-1262.408517	-1262.420935	-1262.424411	-1262.425613
+CV	-1262.774690	-1262.829430	-1262.847811	-1262.854515
(CO) ₅	-565.622853	-565.622853	-565.622853	-565.622853
+ghost Fe	-565.629441	-565.629441	-565.629441	-565.629441
Fe(<i>d</i> ⁶ <i>s</i> ²)	-1262.611517	-1262.634004	-1262.641482	-1262.643951
+CV	-1262.956170	-1263.033345	-1263.064205	-1263.075462
Fe(<i>d</i> ⁶ <i>s</i> ²) ^a	-1262.642195	-1262.657352	-1262.662903	-1262.664752
+CV	-1262.968303	-1263.048859	-1263.080904	-1263.092482
CO	-113.129534	-113.129534	-113.129534	-113.129534
5CO	-565.647670	-565.647670	-565.647670	-565.647670
BSSE on Fe	6.8	3.0	1.3	0.8
+CV	32.1	13.6	5.2	2.1
BSSE on (CO) ₅	4.1	6.5	9.0	12.3
Total BSSE	10.9	9.4	10.3	13.1
+CV	36.2	20.1	14.3	14.4
D_e to Fe(<i>d</i> ⁶ <i>s</i> ²)	187.6	185.9	187.7	191.4
+CV	207.9	198.9	195.5	197.2
BSSE corrected	176.7	176.5	177.4	178.3
+CV	171.7	178.8	181.2	182.8
Relativity corrected ^a	180.1	179.9	180.8	181.7
+CV	175.1	182.2	184.6	186.2
D_0^b	169.7	169.5	170.4	171.3
+CV	164.7	171.8	174.2	175.8
D_e^c	168.4	171.2	174.3	178.3
+CV	200.3	189.2	185.0	186.5
D_0^c	150.5	154.8	157.0	158.3
+CV	157.1	162.1	163.7	165.2
Expt. [12]				136.7

^a Relativity correction +3.4 kcal/mol^b Zero-point correction -10.4 kcal/mol^c Active space includes 4*p* orbital (see text)

numbers; however, this point should not be overemphasized. Even at the CASPT2 level we can see that as the metal basis set is improved the core–valence contribution to binding decreases, which again seems counterintuitive. As we shall see, though, this decrease in the core–valence contribution as the basis set is improved is also observed in Fe(CO)₅ and Cr(CO)₆. Thus it appears that the CCSD(T) results for Ni(CO)₄ are simply more extreme than the other cases, in that the core–valence contribution itself decreases the binding.

3.2 Fe(CO)₅

The CCSD(T) total energies and energy differences for Fe(CO)₅ are given in Table 3. Here again we include results obtained with the smallest Fe ANO set, [5s 4p 3d 2f 1g], and again they are unsatisfactory. The convergence of the BSSE-corrected CCSD(T) binding energy with basis set size is similar to Ni(CO)₄, but here the largest basis result is in very close agreement with experiment. As we noted earlier, extending the basis further would undoubtedly increase the calculated binding energy, which would make the excellent agreement between the present calculations and experiment a

little worse. We note that the relativistic contribution to the binding energy is 3.4 kcal/mol.

The CASPT2 results are a good deal less satisfactory (Table 4). The molecule is significantly overbound at the CASPT2 level, even when proper account is taken of near-degeneracy effects involving the Fe 4*p* orbital [1]. In addition, the CASPT2 calculations seem to overestimate the contribution that 3*s*3*p* correlation makes to the binding: except for the [5s 4p 3d 2f 1g] basis, which is clearly too small to treat the core–valence correlation properly, all calculations show a contribution that is more than twice that of the CCSD(T) calculations and which again seems implausibly large. The best CASPT2 estimate of the binding energy should be the largest basis result, corrected for BSSE and using the atomic result with the enlarged active space in calculating the dissociation limit. This is almost 163 kcal/mol, which is more than 25 kcal/mol larger than either CCSD(T) or experiment. If we were to ignore the contribution of BSSE (or if we were to assume that it was a measure of basis set incompleteness and that the binding energy should thus be even larger than we compute) then the CASPT2 estimate would be at least 40 kcal/mol too high. This is disappointing. It is also disappointing that in that case, unlike Ni(CO)₄ and Cr(CO)₆, the core–valence

Table 5. Cr(CO)₆ CCSD(T) results (total energies in E_h , energy differences in kilocalories per mole)

	Cr basis set (<i>cc</i> -pVTZ on C and O)		
	[6s 5p 4d 3f 2g]	[7s 6p 5d 4f 3g]	[8s 7p 6d 5f 4g]
Cr(CO) ₆	-1722.657130	-1722.665793	-1722.675739
+CV	-1723.058044	-1723.077571	-1723.090709
Cr(<i>d</i> ⁶)	-1043.204389	-1043.208545	-1043.209837
+CV	-1043.588895	-1043.612533	-1043.619957
Cr(<i>d</i> ⁶) + ghost COs	-1043.208099	-1043.210166	-1043.210599
+CV	-1043.605591	-1043.618719	-1043.622180
(CO) ₆	-678.884437	-678.884437	-678.884437
+ghost Cr	-678.895574	-678.899730	-678.906707
Cr(<i>d</i> ⁵ <i>s</i>)	-1043.461553	-1043.465118	-1043.465833
+CV	-1043.844491	-1043.867304	-1043.874175
CO	-113.153719	-113.153719	-113.153719
6CO	-678.922314	-678.922314	-678.922314
BSSE on Cr	2.3	1.0	0.5
+CV	10.5	3.9	1.4
BSSE on (CO) ₆	7.0	9.6	14.0
Total BSSE	9.3	10.6	14.5
+CV	17.5	13.5	15.4
D_e to Cr(<i>d</i> ⁵ <i>s</i>)	171.5	174.7	180.5
+CV	182.8	180.7	184.6
BSSE corrected	162.2	164.1	166.0
+CV	165.3	167.2	169.3
Relativity corrected ^a	169.3	171.2	173.1
+CV	172.4	174.3	176.4
D_0 ^b	157.0	158.9	160.8
+CV	160.1	162.0	164.1
Expt. [13]			153

^a Relativity correction
+7.1 kcal/mol
^b Zero-point correction
-12.3 kcal/mol

contribution to the binding energy is predicted differently by CCSD(T) and CASPT2. CASPT2 has the potential to provide a computationally inexpensive route to calculating the core–valence contribution, because it is much less effort to correlate more inactive electrons in the CASPT2 case than in CCSD(T).

3.3 Cr(CO)₆

CCSD(T) total energies relevant to the binding energy of Cr(CO)₆ are listed in Table 5. As seen before, the BSSE on Cr decreases substantially as the basis set is extended, and even with core–valence correlation included is little more than 1 kcal/mol in the largest [8s 7p 6d 5f 4g] ANO set. However, the BSSE on the CO ligands again increases as the basis is extended, and thus the total BSSE again behaves nonmonotonically as the metal basis set is extended. Our best estimate of the binding energy is more than 10 kcal/mol larger than experiment: a huge discrepancy compared to Ni(CO)₄ and Fe(CO)₅. Nothing in the calculations suggests that Cr(CO)₆ should be more difficult to treat, and it may be that the problem lies with the experimental result.

Core–valence correlation has a similar effect on the binding energy as in Fe(CO)₅, increasing the binding by 4–5 kcal/mol. At the CASPT2 level (Table 6) the core–valence contribution to binding is predicted to be somewhat larger than at the CCSD(T) level, but the difference is much less than 1 kcal/mol. This adds credence to the suggestion made earlier that CASPT2 can be used to obtain a rather reliable estimate of the core–valence contribution. Since the CASPT2 calculations

require considerably less effort than the CCSD(T) calculations, especially when correlation of the metal 3*s*3*p* electrons is included, this is very encouraging. Nevertheless, the discrepancy between the sign of the CCSD(T) and CASPT2 core–valence contributions for Ni(CO)₄ argues for some caution here.

3.4 Calculated binding energies

As we noted at the outset, we chose to apply a counterpoise correction for BSSE. We are aware that this is a contentious issue, and of course our tables include all the uncorrected numbers so that readers who prefer not to make this correction can easily obtain uncorrected numbers. The most important issue is probably not whether or not one should make such a correction, but rather what one can learn about basis set incompleteness from the size of the BSSE correction. Once core–valence correlation is included it is clear that even our largest basis sets are rather far from convergence. From all of the tables it would seem that our largest basis set results are likely to be several kilocalories per mole in error. This is true irrespective of whether one makes a correction for BSSE or not, although the corrected results appear to be somewhat close to converged. In all cases, the calculated binding energies would be expected to increase if the basis set were improved.

What then of the agreement between calculations and experiment? For Ni(CO)₄ our best result is in perfect agreement with experiment, and the computed number would certainly increase if the basis set were improved further. Without the BSSE correction the computed

Table 6. Cr(CO)₆ CASPT2 results (total energies in E_h , energy differences in kilocalories per mole)

	Cr basis set (<i>cc</i> -pVTZ on C and O)		
	[6s 5p 4d 3f 2g]	[7s 6p 5d 4f 3g]	[8s 7p 6d 5f 4g]
Cr(CO) ₆	-1722.549579	-1722.558391	-1722.568349
+ CV	-1722.953715	-1722.974589	-1722.988111
Cr(<i>d</i> ⁵ <i>s</i>)	-1043.452603	-1043.455870	-1043.456452
+ CV	-1043.837486	-1043.861523	-1043.868462
CO	-113.129534	-113.129534	-113.129534
6CO	-678.777205	-678.777205	-678.777205
BSSE from CCSD(T)	9.3	10.6	14.5
+ CV	17.5	13.5	15.4
D_e to Cr(<i>d</i> ⁵ <i>s</i>)	200.7	204.1	210.0
+ CV	212.7	210.8	214.9
BSSE corrected	191.3	193.5	195.6
+ CV	195.3	197.3	199.5
Relativity corrected ^a	198.4	200.6	202.7
+ CV	202.4	204.4	206.6
D_0 ^b	186.1	188.3	190.4
+ CV	190.1	192.1	194.3
Expt. [13]			153

^a Relativity correction
+ 7.1 kcal/mol

^b Zero-point correction
-12.3 kcal/mol

results are significantly too large. Similarly, the results for Fe(CO)₅ are in excellent agreement with experiment after the correction has been made, but are much too large without it. For Cr(CO)₆ our calculated binding energy is much larger than experiment even when the BSSE correction is applied, and without the correction this overestimation is much greater. Improvement in the calculations will almost certainly make matters worse by further increasing the calculated binding energy. It is tempting to conclude that the experimental result for the binding energy of Cr(CO)₆ is too small. A new experimental estimate would be very valuable here.

4 Conclusions

By combining large basis sets with accurate correlation treatments we have obtained very accurate binding energies for the transition-metal carbonyls. Both BSSE and relativity have a nonnegligible effect on the calculated binding energies, although since the respective effects are of opposite sign there will be some cancellation of errors when both are neglected. Core–valence correlation on the metal atom (i.e., correlation of the 3*s*3*p* electrons) has a substantial effect on the binding energy and cannot possibly be ignored. Reliable treatment of this core–valence correlation requires careful attention to the basis set, and we have demonstrated that substantial differences between previously computed binding energies for these systems and the present results derive in large part from limitations of the basis sets used in earlier work in treating core–valence correlation. Although the CASPT2 method does not produce absolute binding energies in as good agreement with experiment as those of CCSD(T), the relative contribution of 3*s*3*p* correlation is given fairly well by CASPT2, at least for Ni(CO)₄ and Fe(CO)₆. This is encouraging because these correlation effects can be calculated very much more cheaply with CASPT2 than with CCSD(T). Finally, we find the disagreement between theory and experiment for the binding energy

of Cr(CO)₆ implausibly large. We suggest that the experimental estimate, which dates from some years ago, is too low, and that this quantity could profitably be re-investigated by experimentalists.

Acknowledgements. This work was supported by the National Science Foundation through grant no. CHE-9700627 and cooperative agreement no. DACI-9619020, and by a grant of computer time from the San Diego Supercomputer Center. The authors acknowledge helpful discussions with Björn Roos and Paul Bagus.

References

- Persson BJ, Roos BJ, Pierloot K (1994) *J Chem Phys* 101: 6810
- Blomberg MRA, Siegbahn PEM, Lee TJ, Rendell AP, Rice JE (1991) *J Chem Phys* 95: 3898
- Barnes LA, Rosi M, Bauschlicher CW (1991) *J Chem Phys* 94: 2031
- Barnes LA, Liu B, Lindh R (1993) *J Chem Phys* 98: 3978
- Andersson K, Malmqvist PA, Roos BO (1992) *J Chem Phys* 96: 1218
- Boys SF, Bernardi F (1970) *Mol Phys* 19: 553
- Werner H-J, Knowles PJ, MOLPRO (a package of ab initio programs) with contributions from Amos RD, Bernhardsson A, Berning A, Celani P, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Hampel C, Hetzer G, Korona T, Lindh R, Lloyd AW, McNicholas SJ, Manby FR, Meyer W, Mura ME, Nicklass A, Palmieri P, Pitzer R, Rauhut G, Schütz M, Stoll H, Stone AJ, Tarroni R, Thorsteinsson T
- Andersson K, Barysz M, Bernhardsson A, Blomberg MRA, Carissan Y, Cooper DL, Fleig T, Fülcher MP, Gagliardi L, de Graaf C, Hess BA, Karlström G, Lindh R, Malmqvist PÅ, Neogrády P, Olsen J, Roos BO, Schimmelpfennig B, Schütz M, Seijo L, Serrano-Andrés L, Siegbahn PEM, Stålring J, Thorsteinsson T, Veryazov V, Wierzbowska M, Widmark P-O (2001) *MOLCAS-5*, Lund University, Sweden
- Widmark P-O, Malmqvist P-Å, Roos BO (1990) *Theor. Chim Acta* 77: 291
- Forsberg N, Malmqvist P-Å (1997) *Chem Phys Lett* 274: 196
- Sunderlin LS, Wang D, Squires RR (1992) *J Am Chem Soc* 114: 2788
- Schultz RH, Crellin KC, Armentrout PB (1991) *J Am Chem Soc* 113: 8590
- Pittam DA, Pilcher G, Barnes DS, Skinner HA, Todd D (1975) *J Less-Common Met* 42: 217