of asymmetric reactions of ketones catalyzed by main group Lewis acids.

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The Ni–CO Binding Energy in $Ni(CO)_x$ (x = 1–4). A Theoretical Investigation

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Abstract: The Ni–CO binding energies have been calculated for the sequence $Ni(CO)_x$ (x = 1–4) with high-accuracy quantum chemical methods. The results obtained in these calculations are 30 kcal/mol (exptl = 29 kcal/mol) for the first carbonyl, 29 kcal/mol (54 kcal/mol) for the second, 36 kcal/mol (13 kcal/mol) for the third, and 24 kcal/mol (25 kcal/mol) for the fourth carbonyl. The calculated total binding energy for $Ni(CO)_4$ is thus 120 kcal/mol (exptl = 120 or 140 kcal/mol), which is a major improvement compared to a previously calculated value of 79 kcal/mol. The main reason for the improvement of the theoretical results is that electron correlation effects for the CO ligand electrons are taken into account in the present calculations, which was not the case in the previous study. For the individual carbonyl binding energies large discrepancies still remain between theory and experiment, however. These discrepancies remain even if very large atomic basis sets are used in the calculations and they are therefore most probably due to an error in the experimental value. To test the adequacy of the present calculations the C–O frequency shift in $Ni(CO)_2$ was also calculated. This is a difficult property to calculate, but reasonable agreement with experiment was still obtained. A strong coupling between the two carbonyl ligands is found to give an important contribution to the C–O frequency shift.

I. Introduction

The transition metal–carbonyl bond is of fundamental importance in both organometallic chemistry and surface chemistry. It has therefore been extensively studied, both experimentally and theoretically, and the bonding mechanism is now essentially understood. A puzzling observation, which still needs further investigation, however, is the irregular trend in the experimentally determined carbonyl binding energies for $Ni(CO)_x \rightarrow Ni(CO)_{x-1} + CO$ for x = 1–4. The binding energies are obtained from a combination of photoelectron spectroscopy measurements by Stevens et al.[1] and appearance potential measurements by Compton and Stockdale[2] on the negative ions $Ni(CO)_x^-$ (x = 1–3). These experiments give a total Ni–CO binding energy of 120 kcal/mol for $Ni(CO)_4$, thus yielding an average Ni–CO binding energy of 30 kcal/mol. The first and the fourth carbonyl groups are bound by 29 and 25 kcal/mol, respectively. This is reasonably close to the average. Surprisingly enough, however, the second carbonyl obtains a much larger binding energy of 54 kcal/mol, and the third carbonyl a very small binding energy of 13 kcal/mol. Previous theoretical investigations[3,4] gave roughly the same binding energy for the first and the second carbonyl, 24 and 27 kcal/mol, respectively.[3] These theoretical results, however, cannot be considered definitive since in particular the discrepancy between the calculated total binding energy of $Ni(CO)_4$ of 79 kcal/mol and the relatively well established experimental value of 140 kcal/mol[6] is very large. In a recent paper[5] on NiCO we showed that the previous results suffered from not correlating all ten CO valence electrons. When all valence electrons are correlated, the binding energy of NiCO increases from 24 to 33 kcal/mol. Since it is likely that ligand correlation is responsible for the major part of the discrepancy between theory and experiments for the total binding energy of $Ni(CO)_4$, we have investigated the effects of ligand correlation on the whole series of binding energies up to $Ni(CO)_4$.

Apart from the rather uncertain dissociation energies, the most accurate experimental data that exist for the series $Ni(CO)_x$ (x = 1–4) is the vibrational frequencies of the IR active CO stretching modes, measured by DeKock[7] in an argon matrix experiment. A larger frequency shift (relative to free CO) is obtained for the antisymmetric stretch in $Ni(CO)_2$ than for NiCO, 171 cm^{-1} compared to 142 cm^{-1}. In a simplified interpretation, where the C–O force constant is taken to be proportional to the vibrational frequency, this result seems to support the larger binding energy obtained experimentally for the second carbonyl group. Thus, as a check of our calculations for the NiCO and $Ni(CO)_2$ binding energies, we have also considered the vibrational frequencies. Since our previous study on NiCO has shown that a reliable shift for the CO stretching frequency can be obtained if all valence electrons are correlated, similar calculations have been performed for $Ni(CO)_2$. However, there are some questions about the impor-

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tance of vibrational couplings: the force constants calculated by Carsky and Dedieu[8] for $Ni(CO)_2$ suggest that only nearest neighbor couplings have to be included, while the work of DeKock[7] suggests that this might not be sufficient. Therefore we also consider how sophisticated a treatment is required to accurately compute the CO stretching frequencies in $Ni(CO)_2$.

In the sequence of calculations on $Ni(CO)_x$ (x = 1–4) standard basis sets were used for nickel, carbon, and oxygen. For NiCO and $Ni(CO)_2$ we have in addition to these calculations also performed calculations using a large ANO (Atomic Natural Orbitals) basis set.[11] All our calculations show that the large discrepancy between theory and experiment remains for the binding energy of the second CO group and is likely to be due to an error in the experimental value.

In the next section we give the computational details and in section III we discuss the results for the CO binding energies in the series $Ni(CO)_x$ (x = 1–4) calculated at different levels of accuracy. In section IV we discuss the calculated frequency shifts for $Ni(CO)_2$ and for NiCO. Finally, in section V we summarize the conclusions and point out some possible explanations to the discrepancy between theory and experiment.

II. Computational Details

We have performed calculations to determine the binding energies of $Ni(CO)_x$ (x = 1–4) and the vibrational frequencies of $Ni(CO)_2$ using different methods. Electron correlation has been included by means of configuration interaction and by means of the coupled pair functional approach. The binding energies are determined for the following reactions: $Ni(CO)_x \rightarrow Ni(CO)_{x-1} + CO$. The NiCO binding energy is calculated relative to the $^3D(3d^94s^1)$ state of the nickel atom. We have used basis sets of double-ζ quality and better, always including a diffuse d function on nickel. For NiCO and $Ni(CO)_2$ calculations were also done with a large ANO basis set. In this section we first describe the geometries used for the binding energy calculations and the procedure used for the calculation of the vibrational frequencies. Thereafter we describe the different methods applied and finally we give the different basis sets used.

(a) Geometries. Most of the binding energy calculations are performed at fixed geometries. The CO distance is then set to 2.17 a_0 which is the experimental CO distance for $Ni(CO)_4$. For the NiC distance in NiCO we used the value 3.28 a_0, which was obtained in a previous study,[3] and for $Ni(CO)_x$ (x = 2–4) we used an NiC distance of 3.50 a_0, close to the value obtained for $Ni(CO)_2$ (3.49 a_0) in the previous study.[3] The experimental NiC distance in $Ni(CO)_4$ is 3.45 a_0 and in the previous study[3] we obtained a value of 3.56 a_0. The binding energy is not very sensitive to the bond distances, e.g., the energy difference between R_{NiC} = 3.50 and 3.60 a_0 in $Ni(CO)_3$ is about 1 kcal/mol (the minimum is at 3.50 a_0). In some cases bond distance optimizations were performed, and the results will be described in the text below.

From experiment[7] it is known that NiCO and $Ni(CO)_2$ are linear, $Ni(CO)_3$ is planar with D_{3h} symmetry, and $Ni(CO)_4$ is tetrahedral.

(b) Vibrational Frequencies. For the linear $Ni(CO)_2$ we have calculated vibrational stretching frequencies using symmetry coordinates. The symmetric force constants were calculated using D_{2h} symmetry, and the antisymmetric force constants were calculated using C_{2v} symmetry. Harmonic force constants were obtained from two-dimensional fits to third-degree polynomials, and the vibrational frequencies were determined by the standard GF matrix method. From combinations of the symmetric and antisymmetric force constants internal force constants were also calculated. In the calculation of the antisymmetric modes using the coupled pair functional methods problems occurred due to the non-invariance of the calculated energies with respect to orbital rotations (see next subsection).

(c) Methods. For the zeroth-order wave function we have performed both SCF (Self-Consistent Field) and CASSCF (Complete Active Space SCF)[12] calculations. In one set of CASSCF calculations all ten valence electrons on nickel were correlated. These CASSCF calculations, denoted CAS10, were performed for all the nickel carbonyls. For NiCO and $Ni(CO)_2$ the sd hybridization in the σ symmetry and the d_π to π^* donation are the most important features of the wave function. For these molecules we therefore also performed a smaller CASSCF calculation, denoted CAS6, where the δ orbitals are omitted from the active space of the CAS10 calculation.

For NiCO and $Ni(CO)_2$ we have performed multireference CCI (contracted configuration interaction) calculations[13] on top of the CASSCF calculations to include the effects of dynamical correlation. The orbitals from the CAS6 calculations were used and all configurations with a coefficient larger than 0.05 in the CASSCF wave function were chosen as reference states, leading to between 7 and 9 reference configurations. In the smallest calculations only the 10 valence electrons on nickel are correlated. These calculations are referred to as CCI10. In the CCI12 calculation for NiCO and CCI14 calculation for $Ni(CO)_2$ also the carbon lone-pair electrons were correlated. We also include the results from a CCI20 calculation on NiCO, correlating all 10 valence electrons on CO, which were described in detail in ref 5, and the results from a CCI10 calculation on $Ni(CO)_4$, previously described in ref 3. All the CCI results reported include the multireference analogue of the Davidson correction.[14]

If correlation of the ligand electrons is to be included for the larger nickel carbonyls a large number of electrons will be correlated and the CI approach will break down due to size inconsistency, i.e., the calculated correlation energy does not scale properly with the number of correlated electrons. Instead we decided to use the size consistent coupled pair functional (CPF) method of Ahlrichs et al.[9] and the modified CPF (MCPF) method of Chong and Langhoff.[10] For this purpose a direct CPF/MCPF program was written. Since these methods are based on a one configuration reference wave function they are not generally applicable to cases with large near degeneracies. In a previous paper[5] we showed that the CPF/MCPF methods give essentially the same results for the NiCO binding energy as the multireference CCI calculations. Since NiCO has the largest near degeneracy effects of the nickel carbonyls we conclude that the CPF/MCPF methods should be adequate for calculating the CO binding energies for the whole series $Ni(CO)_x$ (x = 1–4). In these calculations we correlated the 10 valence electrons on nickel together with all 10 valence electrons on each CO ligand. Thus, in the CPF/MCPF calculations on $Ni(CO)_4$ 50 electrons were correlated.

The CPF/MCPF methods are not invariant to rotations among the occupied orbitals. This is not usually a problem but turned out to cause problems for the calculation of the antisymmetric stretching frequencies for $Ni(CO)_2$. Due to this non-invariance the calculated MCPF potential surface has an artificial bump around the symmetric geometry and the calculated CPF potential surface gave unreasonably low force constants. By a localization procedure it was possible to remove this artefact to a certain extent, so that at least a qualitatively correct force constant is obtained, which is enough for the present purpose. It should be noted that the "non-invariance region" is so large that if this region is simply avoided in the force constant determination the accuracy is severely affected by anharmonic contaminations.

(d) Basis Sets. The main basis set used in this study is the same as the main basis set in ref 5. On nickel this is a Wachters basis set[15] augmented with one diffuse d function and two 4p functions, leading to a 8s,6p,4d contracted basis set. For carbon and oxygen this is the van Duijneveldt 9s,5p set[16] augmented with one polarizing d function leading to 4s,3p,1d contracted basis sets. This basis set will be referred to as basis A and it is used in all the vibrational frequency calculations. Basis B is the same as basis A except that the d functions on carbon and oxygen are removed. Basis B is the only basis set used for $Ni(CO)_4$. Some CASSCF and CCI calculations were performed in a third basis C, which has essentially the same quality as basis B. For nickel basis C is the SDZC-set(1) of Tatewaki and Huzinaga augmented to give a 5s,4p,3d contracted basis set as described in ref 3. The carbon and oxygen basis sets are the same as in basis B.

For NiCO and $Ni(CO)_2$ MCPF calculations were also performed with a large ANO basis set.[11] The nickel basis set is a 19s,14p,10d,6f primitive set contracted to 6s,5p,4d,2f based on the average natural orbitals of the $^3F(3d^84s^2)$, $^3D(3d^9,4s^1)$, and $^1S(3d^{10})$ states of the nickel atom. One diffuse s function and one diffuse p function are added yielding a final contracted basis set of 7s,6p,4d,2f.[17] The basis sets on carbon and oxygen have 13s,8p,6d,4f primitive functions contracted to 4s,3p,2d,1f.[18]

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Table I. Calculated Binding Energies for the Last CO Group in $Ni(CO)_x$ (x = 1–4), CASSCF and CCI Results[d]

	basis A Wachters d on CO	basis C Tatewaki no d on CO	exptl[a]
NiCO:			29 ± 15
CAS6	13	16	
CAS10		22	
CCI10	16	21	
CCI12	24	26	
CCI20	33		
$Ni(CO)_2$:			54 ± 15
CAS6	22	25	
CAS10		26	
CCI10	22		
CCI14	25	27	
$Ni(CO)_3$:			13 ± 10
CAS10		22	
$Ni(CO)_4$:			25 ± 2
CAS10		13	
Total:			120 (140[b])
CAS10		83	
CCI10		79[c]	

[a] Reference 1. [b] The higher experimental value is from ref 6. [c] From ref 3, where a slightly different basis set on CO was used. [d] Energies are given in kcal/mol. The NiCO binding energy is calculated relative to the ^3D state of the Ni atom.

III. The Ni–CO Binding Energies in $Ni(CO)_x$ (x = 1–4)

The experimental binding energies for the CO groups in the nickel carbonyls, given by Stevens et al.,[1] show a very irregular trend. The first CO is bound by 29 kcal/mol, the second by 54 kcal/mol, the third by 13 kcal/mol, and the fourth by 25 kcal/mol. These values are derived from the electron affinities measured by Stevens et al. and the binding energies for the negative carbonyl ions obtained from appearance potentials measured by Compton and Stockdale.[2] As can be seen from Table I the experimental values have large error bars, which stem from the low resolution in the appearance potential measurements on the negative ions. The sum of these binding energies is 120 kcal/mol, which should be compared to earlier thermochemical measurements on $Ni(CO)_4$ yielding a total binding energy of 140 kcal/mol.[6] Stevens et al. predict that the binding energies of NiCO and $Ni(CO)_2$ actually should be higher by about 10 kcal/mol than the values mentioned above. The low intensity of Ni^- and $NiCO^-$ in the appearance potential measurements makes the determination of these two binding energies more uncertain.

In a previous study[3] we obtained a Ni–CO binding energy of 23 kcal/mol for NiCO (relative to the ^3D nickel atom), 27 kcal/mol for the second CO group, and a total binding energy of 79 kcal/mol for $Ni(CO)_4$. The last calculation is of slightly lower accuracy than the calculations on NiCO and $Ni(CO)_2$. In particular for the second CO group the discrepancy between experiment and theory is too large to be acceptable. Several new CASSCF and CCI calculations have therefore been performed and the most interesting results are summarized in Table I. For $Ni(CO)_2$ we also tried bent structures but in all cases the calculated energy was much higher than for the linear structure for which we report results here. In Table II we summarize the results from CPF/MCPF calculations which were performed to include the effects of ligand correlation. For NiCO and $Ni(CO)_2$ we have in addition performed MCPF calculations using a large ANO basis set. These calculations are also included in Table II, and the results show that there are no important effects missing in our smaller basis sets.

In summary the agreement between theory and experiment has improved for NiCO and for the total binding energy of $Ni(CO)_4$ compared to our first calculations.[3] When ligand correlation is included we obtain a binding energy for NiCO of 30–33 kcal/mol and about 120 kcal/mol for $Ni(CO)_4$. However, the discrepancy for $Ni(CO)_2$ still remains, and our best calculated binding energy for the second CO group is 27 kcal/mol, compared to the experimental value of 54 kcal/mol. We further obtain a large deviation from the experimental value for the third CO group, and the calculated value is around 35 kcal/mol compared to the experimental value of 13 kcal/mol. Actually, for the total binding of $Ni(CO)_3$ the agreement between theory and experiment is quite good, the calculated values are in the range 89–96 kcal/mol, and the experimental value is 96 kcal/mol. These results indicate that there is most likely a problem with the experimental determination of the binding energy for the second CO group affecting also the binding energy of the third CO group.

Table II. Calculated Binding Energies for the Last CO Group in $Ni(CO)_x$ (x = 1–4), CPF and MCPF Results[c]

	basis A Wachters d on CO	basis B Wachters no d on CO	basis D large ANO	exptl[a]
NiCO:				29 ± 15
CPF	30	30		
MCPF	30	30	30	
$Ni(CO)_2$:				54 ± 15
CPF	26	29		
MCPF	27	29	27	
$Ni(CO)_3$:				13 ± 10
CPF	34	37		
MCPF	32	36		
$Ni(CO)_4$:				25 ± 2
CPF		24		
MCPF		24		
Total:				120 (140[b])
CPF		121		
MCPF		120		

[a] Reference 1. [b] The higher experimental value is from ref 6. [c] Energies are given in kcal/mol. The NiCO binding energy is calculated relative to the ^3D state of the Ni atom.

Below we discuss the results obtained in the present investigation in more detail.

(a) Ligand Correlation. It is well known that correlation of the d electrons in transition-metal compounds can be very important for obtaining accurate results. For example, the $^1\Sigma^+$ state of NiCO is unbound by 68 kcal/mol at the SCF level (basis A) and bound by 16 kcal/mol in the CCI10 calculation, where the 10 nickel valence electrons are correlated. This correlation effect, however, is to a large extent a near-degeneracy effect. Already in the CAS6 calculation, where the important near degeneracies in the σ and π symmetries are included, NiCO is bound by 13 kcal/mol. In fact, the CASSCF calculations describe dynamic correlation effects surprisingly well. The CAS10 calculations give results in good agreement with the CCI10 calculations. In basis C the binding energy for NiCO at these two levels is calculated to be 22 and 21 kcal/mol, respectively. The CAS10 calculations were carried out for the whole series of $Ni(CO)_x$ (x = 1–4) molecules (basis C). As can be seen from Table I the binding energies calculated at the CAS10 level are smaller than the experimental values, except for the third CO group where the calculated binding energy, 22 kcal/mol, is larger than the experimental value, 13 kcal/mol. The total binding energy of all four CO groups is in this calculation only 83 kcal/mol, compared to the experimental values of 120 and 140 kcal/mol. It is clear that correlation of only the nickel valence electrons does not lead to agreement with the experimental binding energies.

Already in our first paper on NiCO[3] we found that correlation of the carbon lone pair electrons gave an important contribution to the binding energy. In the present basis A this effect is 8 kcal/mol (difference between CCI12 and CCI10). For the second CO group the effect is somewhat smaller, 3 kcal/mol (difference between CCI14 and CCI10). The calculated binding energies, however, are still significantly smaller than the experimental values for both the first and the second CO groups. A rather surprising result from our recent study on NiCO[5] is that correlation of the remaining ligand electrons has a large effect on the binding energy. When all 10 valence electrons on CO are correlated (CCI20) the binding energy of NiCO increases to 33 kcal/mol, in good agreement with the experimental value, 29 kcal/mol. It should be remembered that the experimentally predicted binding energy is somewhat higher than the determined value of 29 kcal/mol.[1] The results for NiCO indicate that ligand correlation could be an important factor missing in our previous description of the binding of the other CO groups.

To describe ligand correlation in the larger Ni(CO)$_x$ molecules we use the size consistent CPF and MCPF methods. The NiCO molecule is expected to lie on the borderline for the applicability of the CPF/MCPF methods. In our previous study[5] we showed that the Ni–C stretching frequency is wrong by more than a factor of 2 in both the CPF and the MCPF calculations compared to the CCI20 result. However, the binding energy of 30 kcal/mol obtained in both the CPF and the MCPF calculations agrees fairly well with the CCI20 result of 33 kcal/mol. Since the near-degeneracy effects are smaller in the larger Ni(CO)$_x$ molecules we expect the CPF/MCPF methods to give reasonably reliable results for all the Ni–CO binding energies in the Ni(CO)$_x$ sequence.

In Table II the results from the CPF/MCPF calculations are summarized. In these calculations we correlate the ten valence electrons on nickel and all ten valence electrons on each CO group. If these results are compared to the CAS10 or the CCI10 results of Table I one can obtain estimates of the importance of ligand correlation of each of the CO groups. For the binding energy of the second CO group ligand correlation has a small effect, only 5 kcal/mol. This is surprising since the effect is as large as 14 kcal/mol for the first CO group. The values for the first and second CO groups are taken from our larger basis set A. For the third and fourth CO groups the effect on the binding energy from ligand correlation can only be estimated through comparisons between the slightly different basis sets B and C, which both lack d functions on carbon and oxygen. The values obtained are about 14 and 11 kcal/mol, respectively. The ligand correlation effect on the total Ni–CO binding energy of Ni(CO)$_4$ is thus calculated to be 40–45 kcal/mol, with a minor contribution from the second CO group.

One can further notice in Table II that the CPF and the MCPF methods give very similar results, and the calculated binding energies differ by at most 2 kcal/mol. This fact increases the reliability of the results, since a discrepancy in the results from the two varieties of the CPF method usually indicates that there is a problem with this type of approach for that case.

(b) Basis Set Effects. As can be seen from Tables I and II the basis set dependence of the Ni–CO binding energies is rather small. We know from other calculations that the Wachters and the Tatewaki–Huzinaga nickel basis sets only differ by about 1 kcal/mol in these types of calculations. Thus the main difference between the basis sets A, B, and C is whether d functions are included on carbon and oxygen or not. In the CASSCF and CCI calculations the d functions on the carbonyl groups decrease the Ni–CO binding energies with 2–5 kcal/mol for the first and the second CO groups. At the CPF/MCPF level there is no difference between the two basis sets for NiCO, but for the second and the third CO groups the d functions decrease the binding energy by 2–4 kcal/mol. The basis set without d functions on the carbonyl groups thus seems to give a superposition error of about 3 kcal/mol for, at least, the second and third carbonyl groups, and it can therefore be concluded that our total binding energy for Ni(CO)$_4$ of 120 kcal/mol contain some basis set superposition energy. However, our experience is that for superposition errors of this magnitude, basis set incompleteness is usually larger. In addition, the one reference CPF/MCPF methods certainly miss some correlation energy due to higher excitations as can be seen on the NiCO results where the large CCI calculation gives 3 kcal/mol larger binding energy than CPF and MCPF. Thus, in spite of the superposition errors we feel that our computed binding energies are lower bounds.

A large ANO basis set (basis D) was also used in MCPF calculations on NiCO and Ni(CO)$_2$. This basis set is very flexible in the valence regions and contains several f functions on nickel and both d and f functions on carbon and oxygen. As can be seen from Table II this basis set gives identical results for the binding energies of the first and second carbonyl groups as our standard basis set A. There are, however, some differences between the results from the two basis sets. The Ni–C distance in Ni(CO)$_2$ obtained at the MCPF level is 3.42 a_0 for the ANO basis set compared to 3.47 a_0 for basis set A. CCI14 also gives 3.47 a_0 for basis set A. It is interesting to note that too long bond distances is a common problem in transition metal complex calculations, the most dramatic example being ferrocene.[25] Also the bond distance in Ni(CO)$_4$ was much too long in our previous calculation.[3] The shortening of the bond distance in Ni(CO)$_2$ obtained by using the large ANO basis set could therefore be a hint of where the problem in the previous calculations has been, namely the use of too inflexible basis sets particularly for the higher l quantum numbers. Also the symmetric Ni–C frequency in Ni(CO)$_2$ differs from the two basis sets, and the ANO basis set gives 403 cm^{-1} and basis A gives 374 cm^{-1} at the MCPF level. Basis set A gives 405 cm^{-1} at the CCI14 level. It should be remembered that the MCPF method does not give an accurate Ni–C frequency for NiCO.[5] For NiCO the ANO basis gives the same Ni–C distance as basis A at the MCPF level, 3.27 a_0. The CCI20 result for basis A is 3.21 a_0.

(c) Comparison with Previous Calculations. No other calculations on the whole series of Ni–CO binding energies exist. Several calculations have been done on NiCO and these were discussed in our recent paper on NiCO.[5] Here we only want to mention a few recent calculations on the total Ni–CO binding energy in Ni(CO)$_4$. Rohlfing and Hay[19] used second-order Møller–Plesset perturbation theory (MP2) and they obtained a too large Ni(CO)$_4$ binding energy of 187 kcal/mol. This is not surprising since the MP2 method is known to be quite unreliable for transition-metal systems. For the nickel atom, for example, MP2 fails completely to describe the electronic spectrum. Also the X$_\alpha$ method gives too large nickel–carbonyl binding energies. Rösch et al.[20] obtained a Ni(CO)$_4$ binding energy of 198 kcal/mol. Also this result is expected since the X$_\alpha$ method is known to give too large binding energies for transition-metal systems. However, a major improvement seems to have been introduced for the X$_\alpha$ methods recently.[21] Ziegler et al.[22] report a Ni(CO)$_4$ binding energy of 129 kcal/mol (the experimental ^{3}D–^{1}S splitting for the nickel atom is used to refer the binding energy to the same asymptotic limit as the rest of the results discussed here). Good agreement with experiment is obtained for a whole series of metal carbonyl compounds in ref 22.

IV. Vibrational Frequencies and Force Constants for Ni(CO)$_2$

The most accurate experimental information available for the Ni(CO)$_x$ series is the CO stretching frequencies for the IR active modes measured by DeKock.[7] As a further check of our calculated CO binding energy in Ni(CO)$_2$ we also have calculated the CO stretching frequency shifts for Ni(CO)$_2$ to be compared to the experimental shifts. The experimental information shows that Ni(CO)$_2$ is linear,[7] and we have calculated the symmetric and antisymmetric force constants and stretching frequencies. The most important result is that our calculated shifts for the CO stretching frequencies relative to free CO are not smaller than the experimental values. Too small shifts would have implied that the carbonyl groups in our calculations were not enough perturbed which would also lead to a too small binding energy. In Tables III and IV we report the CO stretching frequencies, frequency shifts, and force constants for Ni(CO)$_2$. For comparison the corresponding values for NiCO are also given.[5]

We would here like to make some comments as to how the calculations of the vibrational frequencies of Ni(CO)$_2$ were made. Since the highly correlated calculations are quite time consuming we tried to minimize the number of calculations to be done and also to use as much symmetry as possible. It seemed a reasonable approximation to neglect the coupling between the two CO groups

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Table III. Calculated CO Stretching Frequencies for CO, NiCO, and $Ni(CO)_2$ in cm^{-1}

			$Ni(CO)_2$	
	CO	NiCO	symmetric	antisymm.
		Frequencies		
exptl	2138	1996[a]	~2100[b]	1967[a]
SCF	2435	2310	2408	2092
CAS6	2435	2201	2367	1978
CCI14	2481	2284	2503	2113
CPF	2189	2032	2154	
MCPF	2186	2074	2171	~1910
CD[c]	2294	2240	2352	2266
		Shift		
exptl		−142[a]	~−40[b]	−171[a]
SCF		−125	−27	−343
CAS6		−234	−68	−457
CCI14		−197	+22	−368
CPF		−157	−35	
MCPF		−112	−15	~−280
CD[c]		−54	+58	−28

[a] Reference 7. [b] Reference 1. [c] SCF calculations by Carsky and Dedieu.[8]

Table IV. Calculated Internal Force Constants in au

	CO	NiCO	$Ni(CO)_2$	
	k_{CO}	k_{CO}	k_{CO}	$k_{COCO'}$
SCF	1.54	1.38	1.33	0.16
CAS6	1.54	1.25	1.28	0.15
CCI14	1.60	1.35	1.38	0.18
MCPF	1.24	1.12	~1.1	~0.1
CPF	1.24	1.07		
DeKock[a]		1.02	1.07	0.06
CD[b]	1.39	1.28	1.37	0.01

[a] Reference 7. [b] SCF calculations by Carsky and Dedieu.[8]

and only take couplings between atoms that are nearest neighbors into account. If this approximation is valid, i.e., if $k_{CO,CO'}$ is close to zero, and if symmetry coordinates are used in the vibrational analysis, the diagonal force constant element for the antisymmetric CO stretch (k_{CO} - $k_{CO,CO'}$) will have the same value as the symmetric diagonal force constant (k_{CO} + $k_{CO,CO'}$). In previous calculations by Carsky and Dedieu[8] very similar values for the two force constants were indeed obtained. We therefore, in the first step, decided to calculate the CO force constant only for the symmetric mode and use the same value in the calculation of the antisymmetric frequencies. Only the coupling between the two Ni–C stretches (nearest neighbors) was taken into account to give a splitting between the symmetric and antisymmetric CO stretch. This calculation leads to a very small shift for the antisymmetric CO stretch relative to free CO, about 30 cm^{-1} compared to the experimental shift of 171 cm^{-1}, and this result might appear to indicate that our calculated binding energy is too small. However, as noted in the introduction, the work of DeKock suggests that this might not be a sufficient level of treatment for the frequency calculation. We therefore calculated the antisymmetric CO stretching force constant itself and it turns out that the CO force constants for the symmetric and the antisymmetric modes are quite different. Thus, the coupling between the two CO groups is quite large. As can be seen from Table III large shifts were finally obtained for the antisymmetric CO stretch. It should be noted that the extremely small shift first obtained is a combination of the neglect of the CO–CO coupling constant and the use of symmetry coordinates. We finally explicitly calculated all six force constants using symmetry coordinates (for most levels of accuracy).

(a) Vibrational Frequencies. In Table III we have compared our calculated CO frequencies at different levels of accuracy to the experimental values for NiCO and $Ni(CO)_2$. The trends in the experimental frequency shifts are well reproduced by our calculated values. First, the shift for the symmetric CO stretch in $Ni(CO)_2$ is much smaller than the shift for the antisymmetric stretch, and the experimental values are ~40 (ref 1) and 171 cm^{-1}, respectively. Second, the antisymmetric CO stretch in $Ni(CO)_2$ has a larger shift than the CO stretch in NiCO, and the experimental values are 171 and 142 cm^{-1}, respectively. At all levels of accuracy the calculated shifts for the symmetric CO stretch in $Ni(CO)_2$ agree better with experiment than the shifts for the antisymmetric stretch. It should be noted, however, that the experimental antisymmetric CO frequency, measured by DeKock,[7] is the most accurate one whereas the symmetric CO frequency measured by Stevens et al.[1] has large error bars (±80 cm^{-1}).

The SCF, CAS6, and CCI14 calculations all give too large shifts for the antisymmetric stretch in $Ni(CO)_2$, in the range 340–460 cm^{-1}, compared to the experimental value 171 cm^{-1}. It is, however, not expected that these calculations should give very accurate results, since the CO electrons are not correlated. In our previous work on NiCO we showed that correlation of the CO electrons is important for obtaining quantitative results for the CO stretching frequency. The trend in the antisymmetric shift for the SCF, CAS6, and CCI14 calculations is the same as the trend for the corresponding shifts in NiCO: the CAS6 calculation gives the largest shift, the SCF calculation gives the smallest shift, and the CCI14(12) calculation falls in between.

The most accurate calculations for the CO stretch should be the CPF/MCPF calculations where all the CO valence electrons are correlated. For the symmetric CO stretch in $Ni(CO)_2$ the errors in the calculated absolute frequencies are quite small. To be comparable to our calculated harmonic gas-phase frequencies the experimental value given in Table III has to be shifted up by about 30 cm^{-1} due to anharmonicity and matrix effects (cf. ref 5). The discrepancy between the CPF/MCPF calculations and experiment is thus only 20–40 cm^{-1} in the absolute CO frequencies. Consequently, also the experimental symmetric shift of ~40 cm^{-1} is well reproduced in these calculations, the CPF calculation gives 35 cm^{-1}, and the MCPF calculation gives 15 cm^{-1}. For the calculation of the antisymmetric frequencies, however, the noninvariance of the CPF/MCPF methods with respect to rotations among the occupied orbitals caused problems. The localization procedure used to remedy this problem was only partially successful, and we estimate that the calculated antisymmetric CO frequency at the MCPF level is at least 50 cm^{-1} too low. However, the calculated shift of 280 cm^{-1} at the MCPF level shows that the inclusion of ligand correlation makes the theoretical antisymmetric CO frequency shift in $Ni(CO)_2$ approach the experimental value (171 cm^{-1}).

The $Ni(CO)_2$ frequencies listed in Table III are obtained from two-dimensional frequency calculations, i.e., the entire block diagonalized force constant matrix is used. For the antisymmetric CO stretch about 40 cm^{-1} of the shift relative to free CO comes from the coupling to the Ni–C mode in the SCF, CCI14, and MCPF calculations (for the MCPF frequency the Ni–C and off-diagonal force constants are taken from the CCI14 calculation). The corresponding number for the CAS6 calculation is about 100 cm^{-1}. In NiCO the coupling to Ni–C lowered the CO frequency shift by 20 cm^{-1} in the CCI20 calculation.

(b) Internal Force Constants. As can be seen from Table IV the calculated internal CO force constants for NiCO and $Ni(CO)_2$ are very close. For example, at the CCI14 level, the CO force constant is 1.35 au in NiCO and 1.38 au in $Ni(CO)_2$. The corresponding value in free CO is 1.60 au. This result is thus in accordance with our binding energy calculations, yielding rather similar binding energies for the first and second CO groups. An important contribution to the large shift observed for the antisymmetric CO frequency in $Ni(CO)_2$ comes from the large coupling element between the two CO groups, and the coupling element is calculated to be 0.1–0.2 au. A large coupling between two CO groups has also been observed for $Li(CO)_2$,[23] which has a structure similar to $Ni(CO)_2$. As mentioned in the previous paragraph part of the shift comes from the coupling to the Ni–C mode. In Table IV we also compare to force constants derived by DeKock on the basis of isotopic frequency shifts and very simplified force constant–frequency calculations.[7] His internal force constants agree quite well with our best calculations.

In Tables III and IV comparison is made to the only previous frequency calculations on $Ni(CO)_2$.[8] In ref 8 the vibrational frequencies are calculated at the SCF level for the whole sequence $Ni(CO)_x$ ($x = 1$–4), using a rather small basis set, not containing d functions on CO. The results in ref 8 do not agree with our SCF results for NiCO and $Ni(CO)_2$. For all the frequency calculations we have used the reasonably large basis set A and for the free CO frequency our result is much closer to the Hartree–Fock limit of 2431 cm^{-1} (ref 24) than those in ref 8, and our value is 4 cm^{-1} off and their value is 137 cm^{-1} off. The calculation in ref 8 reproduces neither the experimental trend in the shifts between NiCO and $Ni(CO)_2$ nor the relation between the symmetric and antisymmetric shifts in $Ni(CO)_2$. These results show that the frequency shifts for both NiCO and $Ni(CO)_2$ are quite sensitive to the basis set.

V. Conclusions

We have calculated the Ni–CO binding energies in the series $Ni(CO)_x$ ($x = 1$–4). We have shown that correlation of the ligand electrons gives large contributions to the binding energies. When ligand correlation is included in the calculations good agreement between theory and experiment is obtained for the first and the fourth CO groups. Also the calculated total Ni–CO binding energies of $Ni(CO)_3$ and $Ni(CO)_4$ agree fairly well with experiment. However, the large discrepancy between theory and experiment remains for the binding energy of the second carbonyl, and we calculate 27 kcal/mol while 54 ± 15 kcal/mol is obtained experimentally. Further, for the third carbonyl we calculate a larger binding energy, about 35 kcal/mol, than the experimentally obtained value, 13 ± 10 kcal/mol. The use of large ANO basis sets on NiCO and $Ni(CO)_2$ does not change the calculated binding energies. In summary, theory predicts a much more regular trend in the carbonyl binding energies in $Ni(CO)_4$ than what is obtained from experiment. For $Ni(CO)_2$ we have also calculated the shifts in the CO stretching frequencies relative to free CO. The calculated shifts agree quite well with accurate frequency measurements.

In trying to find an explanation for the discrepancy between theory and experiment for the second and third carbonyl binding energies one should note the following. On the basis of the results presented in this paper it can be ruled out that any improvements of the general quality of the calculations in terms of basis sets and correlation treatment would lead to significant changes in the calculated binding energy trend. The only way to change the theoretical result seems to be if a different state or a different geometry of $Ni(CO)_2$ could be found to have a lower energy than the linear $^1\Sigma_g^+$ state treated in the present investigation. However, all calculations on bent geometries and on other states of $Ni(CO)_2$ performed so far have resulted in much higher energies than for the linear $^1\Sigma_g^+$ state. It should also be remembered that the IR measurements[7] indicate that the molecule is linear. We therefore conclude that the most likely source for the disagreements is an error or a misinterpretation in the experimental determination of the Ni–CO binding energies.

The experimental values for the Ni–CO binding energies are obtained from a combination of two sets of measurements. One is the measurement of the appearance potentials for the negative ions and the other is the measurement of the electron affinities of the neutral species. One possible error source could be if the two measurements were not made on the same states or structures, i.e., if an excited state would be involved in the measurements for one or more species. For example, if it could be shown that the electron affinity measurements are made on an excited state of $Ni(CO)_2^-$, with an excitation energy of about 1 eV the discrepancy between theory and experiment could be completely explained, for both the second and the third carbonyl group. We are presently investigating the structure of $Ni(CO)_2^-$ and preliminary calculations indicate that the geometry might be bent. If this is the case it might be that the electron affinity measurements involve an excited linear state, since this structure would be likely to have a larger transition probability to the linear $Ni(CO)_2$. Most likely the full explanation for the discrepancy between theory and experiment will involve a combination of several effects. It should also be remembered that the experimental values for the carbonyl binding energies have large error bars.

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