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## Excited States of the Nickel Carbonyls Ni(CO) and Ni(CO)<sub>4</sub>

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**On the Excited States of the Nickel Carbonyls Ni(CO) and Ni(CO)<sub>4</sub>: Challenging Molecules for Electronic Structure Theory**

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3 **On the Excited States of the Nickel Carbonyls Ni(CO) and Ni(CO)<sub>4</sub>: Challenging**  
4 **Molecules for Electronic Structure Theory**  
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16 **Abstract**

17 We apply a wide range of correlated electronic structure approaches to the excited states of  
18 Ni(CO)<sub>4</sub> and Ni(CO) as model complexes of saturated and unsaturated transition metal  
19 carbonyls respectively to understand the performance of each method, in addition to setting  
20 benchmark data for these metal carbonyls. In particular we apply the coupled-cluster linear  
21 response hierarchy, complete-active-space self-consistent field theory, N-electron valence  
22 state multi-reference perturbation theory, Monte-Carlo configuration interaction, and time-  
23 dependent density functional theory with a range of functionals and basis sets. We find that  
24 although the systems can qualitatively be described by a single configuration, that electron  
25 correlation effects are sufficiently strong to give large singles amplitudes in cluster  
26 expansions, which cause spurious solutions to the response equations for the intermediate  
27 CCn methods. DFT also performs well if care is taken to choose an appropriate functional,  
28 although for Ni(CO) several popular functionals give the incorrect ground spin-state,  
29 depending on the amount of Hartree-Fock exchange.  
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## Introduction

Binary transition metal carbonyls are perhaps some of the most intensely investigated groups of molecules. These are paradigm complexes for basic models of metal-ligand bonding, i.e. dative bonding and  $\pi$ -back-bonding. They thus represent very well studied systems, both experimentally and theoretically. A particular area to receive much recent attention is their excited electronic states and resulting reactive photochemistry. Early work on their spectroscopy presented a simple yet elegant understanding of the transitions based on qualitative molecular orbital pictures. However, experimental resolution was very poor, the spectra often appearing broad and featureless. In recent years modern time-resolved pump-probe spectroscopy has revisited their photochemistry, with several unexpected surprises in store. For example,  $\text{Cr}(\text{CO})_6$ ,  $\text{Mn}_2(\text{CO})_{10}$ , and  $\text{Fe}(\text{CO})_5$  all undergo an extremely fast (<100fs) dissociation event (CO loss for  $\text{Cr}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$ , and either Mn-Mn bond cleavage or CO loss for  $\text{Mn}_2(\text{CO})_{10}$ ) followed by rapid radiationless decay to the ground electronic state of the (now) unsaturated complex, to then display highly mode-specific vibrational coherences in this ‘hot’ photoproduct.<sup>1-5</sup> However,  $\text{Ni}(\text{CO})_4$  displays a red luminescence on a much longer timescale following excitation.<sup>5</sup>

Central to furthering our understanding these complex phenomena has been the application of high-level quantum chemical methods to their photophysics and photochemistry. Complete active-space self-consistent-field (CASSCF) theory has seen much use in understanding the reactive photochemistry of such species, and has shown that radiationless decay is associated with Jahn-Teller type conical intersections connecting the excited and ground state potential energy surfaces. Further, semi-classical and quantum wavepacket dynamics simulation has been successfully used to investigate the vibrational coherences observed in the photoproducts.<sup>6,7</sup> However, emerging are the challenges faced in accurately describing the excitation manifolds in such species, and the urgent need to have systematic studies of electron correlation effects and benchmark data for these systems.<sup>8,9</sup> There have been a few pioneering applications of high-level correlated methods to specific systems including CASPT2 to  $\text{Cr}(\text{CO})_6$  and  $\text{Ni}(\text{CO})_4$ ,<sup>10,11</sup> EOM-CCSD to  $\text{Cr}(\text{CO})_6$ ,<sup>12</sup> and LR-CCSD to  $\text{Fe}(\text{CO})_5$ .<sup>1</sup> For  $\text{Cr}(\text{CO})_6$ , CASPT2 proves to be a reliable method to assign the experimental spectrum. The excitations calculated show that the lowest electronic transitions do not correspond to previously assigned ligand field transitions, but instead they correspond to spin or orbitally forbidden charge transfer states. The extensive coupled cluster study on the photochemistry of  $\text{Cr}(\text{CO})_6$  revealed further discrepancies between the experimental and theoretical results.<sup>12</sup> For example, the shoulder observed at 3.9 eV, originally assigned as a

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3 ligand field state, but questioned with CASPT2 as either originating from an MLCT state, or  
4 possibly as an artefact of basis set error, was shown to definitively be MLCT in character.  
5 There have also been several time-dependent density functional theory (TD-DFT) studies.<sup>10,13</sup>  
6 TD-DFT offers the possibility of a very low cost, yet accurate treatment of many excited  
7 states in such systems. However, a wide-range of accuracy versus exchange correlation  
8 functional chosen is seen.  
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13 A systematic approach to excited electronic states is possible through the machinery of  
14 response theory applied to correlated reference wavefunctions. The most successful approach  
15 is the coupled cluster (CC) response hierarchy: CCS, CC2, CCSD, CC3, CCSDT, ... Here  
16 each subsequent CC model systematically improves the description of electron correlation  
17 (through the next order in the fluctuation potential) but with an increase in the power of the  
18 polynomial scaling of model with system size, e.g., CC2 to CCSD the accuracy improves  
19 from 2<sup>nd</sup> to 3<sup>rd</sup> order for the ground state energy, and from 1<sup>st</sup> to 2<sup>nd</sup> order in the associated  
20 response functions, while the scaling goes from N<sup>5</sup> to N<sup>6</sup> (N being proportional to the number  
21 of orbitals). The intermediate models CC2<sup>14</sup> and CC3<sup>15</sup> represent lower cost approximations  
22 to CCSD and CCSDT respectively, obtained by keeping only the lowest non-vanishing order  
23 term(s) from perturbation theory, and enforcing singles to be treated as zeroth-order both with  
24 and without the external perturbation via a T<sub>1</sub> similarity transformation of all operators in the  
25 CC equations. LR-CC theory is closely related to the equation of motion (EOM) approach,  
26 being formally equivalent for excitation energies for the complete models such as CCSD and  
27 CCSDT, while transition moments are more accurate with LR-CC,<sup>16</sup> although the difference  
28 is often negligible.<sup>17</sup>  
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33 Thus, the application of such methods, and their comparison with multireference  
34 approaches is invaluable in assessing the cost and accuracy portfolio available when studying  
35 the excited states of transition metal complexes. Nickel carbonyls make excellent models for  
36 this as they are notionally closed-shell ground state species (*vide infra*) with filled d-shells.  
37 Indeed titanium and nickel carbonyls should be the first target of benchmarking before the  
38 intervening first-row metal carbonyls with more complicated partially filled d-shells. We have  
39 set out to study in detail a saturated and unsaturated species, namely Ni(CO)<sub>4</sub> and Ni(CO)  
40 respectively, both of which have been subject of intense experimental investigation through  
41 the years.  
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46 The electronic absorption spectra of Ni(CO)<sub>4</sub> has been reported previously in the near  
47 UV in the gas phase,<sup>18,19</sup> and similar to other binary carbonyls, is poorly resolved, and lacking  
48 in spectral detail. Both gas and solution phase spectra contain one broad band at 6.0 eV with  
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shoulders slightly lower in energy at 5.5 eV and 5.2 eV in solution, and 5.4 eV and 4.6 eV in the gas phase. All of these transitions are thought to be  $^1A_1 \rightarrow ^1T_2$  metal-to-ligand charge transfer states. Various theoretical attempts have been made to study the excited states of  $Ni(CO)_4$  including the INDO/S method,<sup>18</sup> CASSCF/CASPT2,<sup>11</sup> and TD-DFT<sup>13</sup> with mixed levels of success. For example, it was found that CASSCF overestimated excitation energies on average by over 1 eV.

$Ni(CO)$  has been also studied extensively due to its role as a fundamental model for unsaturated transition metal carbonyls important in many areas of catalysis, where it has been assumed to offer a simple model of chemisorption in catalytic activation processes. The sigma bonding and  $\pi$ -backbonding to the nickel atom has been discussed over the years, since they represent the pillars of the formation of such transition metal complexes. Several theoretical studies of the electronic structure of  $Ni(CO)$  have been performed, firstly focussing on the nature of the ground electronic state. Initially predicted to be an open-shell triplet state,<sup>20</sup> more recent calculations have in fact shown that the ground state is a closed-shell singlet ( $\Sigma^+$ ).<sup>21-23</sup> Different computational methods have been used to describe both the ground state electronic structure, and the respective minimum geometry of  $Ni(CO)$  including DFT,<sup>24</sup> coupled cluster,<sup>25-27</sup> CASSCF,<sup>28,29</sup> and CASPT2.<sup>28</sup> High-resolution spectroscopic characterisation gives a linear structure with a Ni-C distance of 1.669Å and C-O distance of 1.153Å.<sup>24</sup> The properties and vibrational spectrum of the isolated molecule were calculated by Sunderlin et al.<sup>30</sup> Persson et al performed an extensive study on the ground state of metal carbonyls including  $Ni(CO)$ ,<sup>28</sup> where they calculated the binding energies and bond lengths using different degrees of correlated computational approaches and one-electron basis sets, with CCSD(T) in a large basis giving the closest value to the experimental binding energy (34 kcal mol<sup>-1</sup> vs 41±6 kcal mol<sup>-1</sup> for experiment<sup>30</sup>).

The excited states of  $Ni(CO)$  were initially investigated by Madhavan et al in using a basic CI approach.<sup>31</sup> Most recently CCSD, CCSD(T) and EOM-CCSD were used to look at the structure and harmonic vibrational frequencies of the low lying excited electronic states of  $Ni(CO)$  with a range of large basis sets.<sup>26</sup> This revealed the geometry and electronic properties of the first excited states of the molecule where eight different electronic states,  $^3\Delta$ ,  $1^3\Sigma$ ,  $1^3\Phi$ ,  $1^3\Pi$ ,  $2^3\Pi$ ,  $1^1\Delta$  and  $1^1\Pi$  were all computed to have linear equilibrium structures. CCSD(T) seems to perform very well being able to accurately describe the bond lengths and harmonic frequencies for the lowest states of each symmetry. In this study it was concluded that in all these excited electronic states the  $\sigma$  donation for the CO is much less important than the  $\pi$  back donation from the metal in terms of the overall stability of the complex.

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3 Given the on-going importance of such basic metal carbonyls it is a suitable moment to  
4 perform a systematic study of both Ni(CO) and Ni(CO)<sub>4</sub> in terms of the ground state  
5 electronic structure, but more importantly in terms of benchmarking various excited state  
6 methods for such paradigm complexes. Below we apply the LR-CC hierarchy, time-  
7 dependent density functional theory, CASSCF, multi-reference perturbation theory  
8 (NEVPT2), and Monte Carlo configuration interaction to these problems.  
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### 13 14 **Computational details**

15 All (TD)-DFT, (EOM)-CCSD CASSCF calculations were performed with Gaussian 09,<sup>32</sup>  
16 while Dalton2015 was used for all LR-CC and NEVPT2 calculations.<sup>33,34</sup> Ni(CO)<sub>4</sub> and  
17 Ni(CO) were initially optimised in their <sup>1</sup>A<sub>1</sub> and <sup>1</sup>Σ<sup>+</sup> electronic ground states, in T<sub>d</sub> and C<sub>∞v</sub>  
18 point groups with B3LYP in conjunction with the cc-pVTZ basis set.<sup>35,36</sup> In DFT geometry  
19 optimisation all default integration grids and step-sizes were employed.  
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24 For the LR-CC calculations on Ni(CO)<sub>4</sub> the cc-pVDZ basis was used, while for Ni(CO)  
25 a cc-pVTZ basis was used on all atoms. For all coupled cluster calculations a frozen core of 7  
26 orbitals was employed (1s for carbon and oxygen, 1s2p for nickel). A larger frozen of 11  
27 orbitals was also considered but the effect of the frozen core size on excitation energies was  
28 very small (~0.1 eV). The T<sub>1</sub> diagnostic of Lee et al was computed for Ni(CO) and Ni(CO)<sub>4</sub> at  
29 the CCSD level.<sup>37,38</sup>  
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34 For CASSCF calculations two different active spaces were constructed. Firstly (10,11)  
35 active space was used comprising ten electrons in the 3d orbital shell of nickel distributed  
36 among five 3d orbitals plus an additional set of d orbitals representing the 4d ‘anti-bonding’  
37 equivalents of the 3d orbitals. This process of ‘orbital doubling’ of the d orbitals was first  
38 used by Persson et al<sup>28</sup> to introduce further correlation into the active space to better describe  
39 dative electron pair bonding through the associated dynamical correlation achieved through  
40 the extra node in the internuclear metal-ligand region. This has proved to be important in  
41 some of our previous studies using CASSCF to study the photochemistry of transition metal  
42 complexes.<sup>1,39</sup> Finally, a 4s orbital for nickel was also included in the active space. This active  
43 space is to be expected to qualitatively (and semi-quantitatively) describe the ground and low-  
44 lying excited states of Ni(CO)<sub>4</sub> and Ni(CO) based on previous CASSCF studies of other first  
45 row transition metal carbonyls.<sup>1,6,7,39-42</sup> However, for quantitative excitation energies a  
46 balanced treatment of dynamical correlation is required, such as is obtained through  
47 appropriate multireference perturbation theories. As discussed above CASPT2 has previously  
48 been applied to Ni(CO)<sub>4</sub> with success. We decided to apply the N-electron valence space  
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3 perturbation theory at second-order (NEVPT2) to the problem of the excited states of  
4 Ni(CO)<sub>4</sub>.<sup>43-46</sup> This variant of multi-reference perturbation theory is very powerful and  
5 completely avoids any problems of intruder states in the perturbation series. The reference  
6 space for Ni(CO) was constructed (utilising the C<sub>2v</sub> subgroup of C<sub>∞v</sub>) by having the lowest (1-  
7 9) a<sub>1</sub>, (1-3) b<sub>1</sub>, and (1-3) b<sub>2</sub> orbitals doubly occupied in all configurations, with 12 electrons  
8 distributed across the next (10-14) a<sub>1</sub>, (4-6) b<sub>1</sub>, (4-6) b<sub>2</sub>, and 1 a<sub>2</sub> orbitals. NEVPT2  
9 wavefunctions were then evaluated using symmetry for the lowest singlet and triplet states of  
10 each irrep with the cc-pVTZ basis.  
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16 Finally, we have applied Monte Carlo configuration interaction (MCCI) to Ni(CO),  
17 both to confirm the nature of the ground state, and to examine the excited electronic states.  
18 MCCI is a stochastic method that seeks to approximate a full CI wavefunction by discarding  
19 or keeping randomly generated configurations to obtain very compact variational CI  
20 wavefunctions.<sup>47,48</sup> MCCI is very good at treating static correlation but with an appropriate  
21 cut-off can treat both dynamical and static correlation in a balanced manner. MCCI has been  
22 successfully applied to a range of areas including dissociative potentials,<sup>49,50</sup> arbitrary excited  
23 electronic states,<sup>51,52</sup> electric multipole moments,<sup>53</sup> dynamic response properties,<sup>54</sup> core-hole  
24 states,<sup>55</sup> and problem cases in molecular electronic structure theory, such as metal-metal  
25 bonding, and quantifying multireference character.<sup>56,57</sup> As such it is very informative to  
26 contrast the stochastic MCCI scheme with more traditional methods such as outlined above.  
27 Here we have chosen a cut-off c<sub>min</sub>=3x10<sup>-4</sup> based on previous experience with the MCCI  
28 algorithm, and frozen 11 core orbitals from the configuration expansion. We also discuss a  
29 recently introduced measure of multireference character (MR) defined as,  $MR = \sum_i |c_i|^2 - |c_i|^4$ ,  
30 which has limiting values of zero, for a single-configuration wavefunction, and one for the  
31 most strongly multireference system.<sup>56,57</sup> In a configuration interaction expansion one finds  
32 that the value of MR is around 0.3 for an essentially single-reference system (e.g., ground  
33 state hydrogen fluoride at equilibrium), whereas a strongly multireference system (e.g, Cr  
34 dimer ground state) has MR around 0.9. MCCI calculations on Ni(CO) used the same  
35 geometry as the CC and DFT calculations, while the cc-pVDZ and cc-pVTZ(D) bases were  
36 employed. In the latter the f angular momentum functions are removed from the carbons and  
37 oxygens, while g angular momentum functions are removed from the nickel.  
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## 55 **Results and Discussion**

### 56 **Ground State - Ni(CO)<sub>4</sub>**



The structure of Ni(CO)<sub>4</sub> is known to be tetrahedral (T<sub>d</sub> point group) with the ground state being the closed-shell <sup>1</sup>A<sub>1</sub> state.<sup>11,13,58</sup> Table 1 below presents our results for the structure of Ni(CO)<sub>4</sub>, where DFT, CCSD, and CASPT2 all agree well with each other, and with experiment. The electronic structure can be qualitatively understood in terms of the well-known molecular orbital diagram for tetrahedral π-bonded complexes. This MO picture has been discussed extensively by Bauschlicher et al.<sup>59</sup> Although there is mixing of the metal and ligand orbitals one can still qualitatively think of the electronic structure as Ni 3d<sup>10</sup>. We note that the CCSD T<sub>1</sub> diagnostic is 0.0316. This is large enough to indicate some multireference character in the Hartree-Fock orbitals,<sup>57</sup> however the system appears qualitatively well described a single-configuration. For example, many single reference approaches describe the ground state geometry very accurately (Table 1).

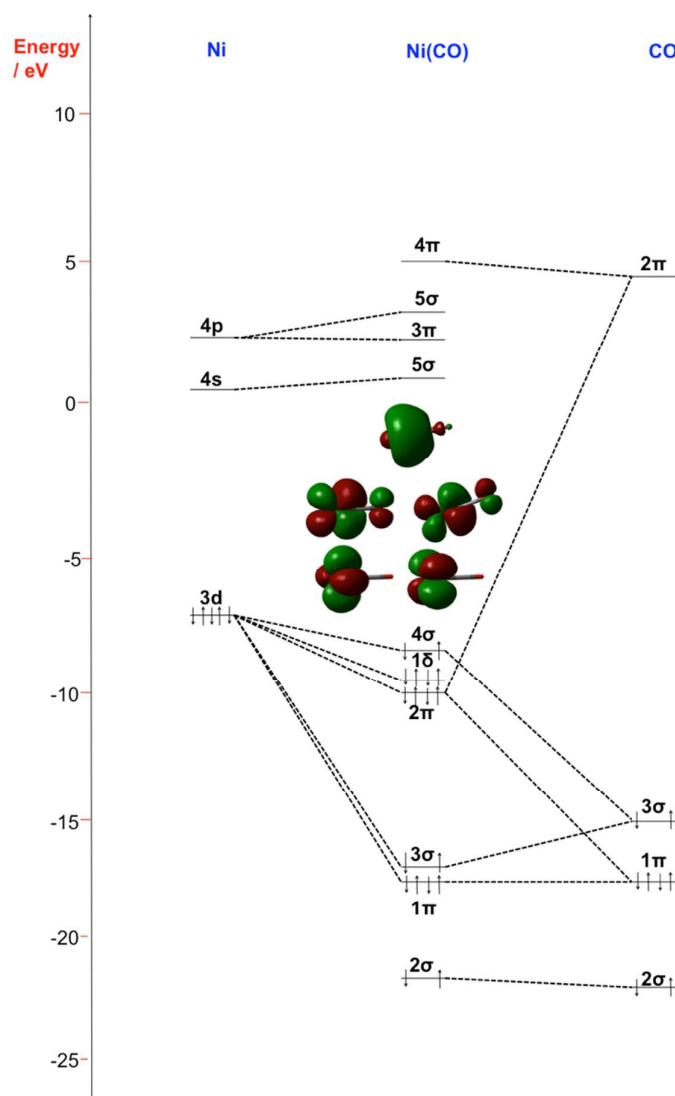
**Table 1.** Ni(CO)<sub>4</sub> optimised geometrical parameters in T<sub>d</sub> symmetry.

Method	Ni-C (Å)	C-O (Å)
CCSD/cc-pVTZ	1.831	1.147
B3LYP/cc-pVTZ	1.846	1.136
MN12L/cc-pVTZ	1.819	1.131
MN12SX/cc-pVTZ	1.823	1.131
CASPT2 <sup>28</sup>	1.830	1.160
Experimental <sup>58</sup>	1.838	1.142

### Ground State - Ni(CO)

The unsaturated Ni(CO) molecule presents a much sterner challenge in terms of the ground electronic state. This was originally thought to be a triplet, but the most recent calculations show it to be a closed-shell singlet (<sup>1</sup>Σ<sup>+</sup>). We further confirm this to be the case with a wide-range both single- and multireference correlated approaches below.

A semi-quantitative (HF/cc-pVTZ) molecular orbital diagram is shown in Figure 1. The singlet-triplet gap is shown in Table 2 for a variety of methodologies, obtained as the difference between the optimised singlet and triplet geometries. The ground spin-state and geometry is clearly very sensitive to electron correlation. In particular for DFT ones finds that hybrid functionals tend to either predict an incorrect triplet geometry and/or spin-state ordering. The degree of (exact) Hartree-Fock exchange appears to be the crucial quantity to correctly describing the singlet spin-state, even with modern meta-GGA functionals such as the Minnesota family. Interestingly CAM-B3LYP correctly describes the triplet geometry and state ordering. The optimised linear singlet geometries are shown in Table 3. Electron correlation causes a contraction in N-C bond length, although the C-O distance is very insensitive to this.



**Figure 1.** Ni(CO) HF/cc-pVTZ MO diagram.

**Table 2.** Ni(CO) singlet-triplet gaps for various methods. Both spin-states optimised with cc-pVTZ basis. Positive/negative sign indicates singlet/triplet more stable than triplet/singlet.

Method	Singlet Geometry	Triplet Geometry	$\Delta E_{ST}$ / eV
HF	Linear	Linear	-2.290
MP2	Linear	Linear	3.595
CCSD	Linear	Linear	0.360
BD	Linear	Linear	0.437
B3LYP	Linear	Bent	1.235
CAM-B3LYP	Linear	Linear	1.790
M06-L	Linear	Linear	1.340
M06-2X	Linear	Bent	-0.300
MN12-L	Linear	Linear	3.224
MN12-SX	Linear	Bent	1.614
CASSCF	Linear	Linear	0.250

**Table 3.** Ni(CO) optimised lowest singlet state geometries for linear structure using cc-pVTZ basis.

Method	Ni-C (Å)	C-O (Å)
HF	1.756	1.112

MP2	1.640	1.174
CCSD	1.670	1.145
BD	1.667	1.139
CCSD(T) <sup>27</sup>	1.687	1.166
B3LYP	1.683	1.149
CAM-B3LYP	1.679	1.142
M06L	1.669	1.156
M06-2X	1.724	1.138
MN12-L	1.673	1.145
MN12-SX	1.680	1.144
CASSCF <sup>29</sup>	1.683	1.161
CASPT2 <sup>28</sup>	1.680	1.170
Experimental <sup>24</sup>	1.669	1.153

The CCSD/cc-pVTZ  $T_1$  diagnostic is 0.0459 indicating caution as a (partially) multireference wavefunction. Similar to its saturated counterpart the electronic structure appears at to contain a dominant component with Ni  $3d^{10}$  character. Multiconfigurational approaches confirm this, with, for example, CAS(10,11) indicating that this dominant configuration accounts for ~86% of the wavefunction. CASSCF further confirms the ground state as a singlet, as does MCCI (*vide infra*) and NEVPT2 (Table 4).

NEVPT2 is one of the most promising and robust of multi-reference perturbation theories, with a number of desirable properties including the absence of intruder states, spin-adapted eigenfunctions, and excited states treated at the same level of accuracy as ground states.<sup>43-46</sup> In table 4 we show results for NEVPT2 state energies, with a reference space built as described above, for each irrep of  $C_{2v}$  symmetry, for the lowest singlet and triplet states. The state energies are converted to labels of the full  $C_{\infty v}$  point group. In table 4 we quote the results of the partially contracted variant of NEVPT2 relative to the totally symmetric singlet state.

**Table 4.** Ni(CO) NEVPT2/cc-pVTZ singlet and triplet state energies.

State	Energy / eV
$1^1\Sigma^+$	0.00
$1^1\Delta$	1.14
$1^1\Pi$	2.54
$1^3\Delta$	0.80
$1^3\Pi$	2.38

### Excited States – Ni(CO)<sub>4</sub>

The vertical excited state energies of Ni(CO)<sub>4</sub> computed with the coupled cluster response hierarchy are presented in Table 5. Ni(CO)<sub>4</sub> is a challenging case in transition metal spectroscopy, as discussed above, in part due to the density of states, with >20 states lying with ~1.2 eV (accounting for all components of degenerate states). In Table 5 we list the lowest six electronic states up to 5.6 eV (EOM-CCSD), which includes 17 component states. Only T<sub>2</sub> symmetry states are dipole allowed, all others being dark states. All low-lying states, and in particular the two bright states observed experimentally have MLCT character, i.e., from the filled Ni 3d orbitals to predominately orbitals of π\* character with largest amplitudes on the carbonyls. The first bright state (1 <sup>1</sup>T<sub>2</sub>) principally involves transitions from the highest filled t-symmetry ligand-field d-orbitals to the lowest empty t-symmetry π\* orbitals, while the second bright state (2 <sup>1</sup>T<sub>2</sub>) principally involves transitions from the same highest filled t-symmetry ligand-field d-orbitals to the next lowest empty e-symmetry π\* orbitals.

Experimentally the gas-phase absorption spectrum shows features at 4.5 eV and 5.2-5.4 eV that are thought to arise from different electronic transitions.<sup>18,19</sup> Of the correlated wavefunction approaches LR-CCSD gives the closest excitations to these, differing by 0.3-0.5 eV. TD-CAM-B3LYP excitation energies are even closer to the two band maxima, although it must be noted that direct comparison between these experimental features with vertical excitation energies is not ideal as the spectrum is very broad; one would ideally like to include vibronic coupling effects, and use larger one-electron basis sets.

The performance of the lower cost methods is interesting and highlights that caution must be exercised when applying them to transition metal complexes such as this. There is clearly no smooth convergence of excitation energy for any state with quite large oscillatory behaviour across the LR-CC series. The uncorrelated CCS fortuitously gives excitation energies close to the CCSD ones, and indeed closer to experiment, although transition strengths for the two brightest are ordered incorrectly. The lower cost doubles methods fair particularly poorly in comparison to the complete CCSD models. Both the iterative CC2 and non-iterative CIS(D) significantly underestimate the excitation energies, often by several eV. We note that for some of the higher excited states we were unable to get the CC2 excitation energies to converge. The poor performance of these doubles models has been discussed in terms of T<sub>1</sub> amplitudes for metal oxides (*vide supra*) and this also causes problems for this metal complex. The failure is not quite as severe as for the unsaturated Ni(CO) discussed below although differences between CC2 and CCSD excitation energies of over 3 eV means that for this molecule CC2 is giving essentially unphysical results (as are very apparent for the

metal oxides and Ni(CO) below with negative excitation energies). This aspect is discussed further below as it is even more problematic for Ni(CO).

The inclusion of connected triples through the non-iterative CCR(3) model also shows large effects but in the opposite direction, i.e., larger excitation energies consistent with an overall oscillatory pattern in the LR-CC series. The magnitudes of the deviations from CCSD are again quite large, although smaller than those of CIS(D), indicating a probable slow oscillatory convergence in the LR-CC series. The perturbative triples changes the ordering of the first bright and adjacent dark states, and generally compresses the excitation range for all states considered.

In terms of low cost methods the performance of the TD-CAM-B3LYP is very encouraging. Designed specially to handle charge transfer (CT) excitations, those investigated here provide an interesting test of this capability, all having very significant CT character. The only discrepancy with LR-CCSD is between the bright  $2^1T_2$  and dark  $3^1T_1$  states in which the ordering is inverted.

**Table 5.** Singlet excitation energies of Ni(CO)<sub>4</sub> in CC hierarchy using cc-pVDZ basis. Oscillator strengths for bright states are given in parenthesis..

State	Character	CCS	CIS(D)	CC2	LR-CCSD	EOM-CCSD	CCR(3)	CAM-B3LYP
$1^1T_1$	MLCT	4.628 (0.0000)	3.282	2.047	4.715 (0.0000)	4.715 (0.0000)	6.011	4.472 (0.0000)
$1^1E$	MLCT	4.831 (0.0000)	3.218	1.932	4.752 (0.0000)	4.752 (0.0000)	6.031	4.665 (0.0000)
$1^1T_2$	MLCT	5.138 (0.1035)	3.284	1.361 (0.490)	5.051 (0.0550)	5.051 (0.0542)	6.306	4.976 (0.036)
$2^1T_1$	MLCT	5.548 (0.0000)	2.847	-	5.132 (0.0000)	5.132 (0.0000)	6.298	4.896 (0.0000)
$3^1T_1$	MLCT	5.822 (0.0000)	2.944	-	5.374 (0.0000)	5.374 (0.0000)	6.640	5.427 (0.000)
$2^1T_2$	MLCT	6.121 (0.0819)	2.841	1.979 (0.015)	5.564 (0.0780)	5.564 (0.0805)	6.611	5.266 (0.0656)

### Excited States – Ni(CO)

Our vertical excited state energies for Ni(CO) are presented in Table 6a and b for cc-pVDZ and cc-pVTZ bases respectively. Considering first LR-CCSD, the first excited electronic state is the dark  $1^1\Delta$  state corresponding to transitions from off-axis  $\delta$ -symmetry pure Ni d-orbitals to a  $d_\sigma$  Ni-carbonyl anti-bonding orbital. In going from cc-pVDZ to cc-pVTZ the excitation energy increases by around 0.2 eV. The next state is the first bright state ( $1^1\Pi$ ), which has a very small oscillator strength. This state involves transitions from Ni-carbonyl  $\pi^*$  orbitals (analogues of those involved in the MLCT states of Ni(CO)<sub>4</sub> above) to the same  $d_\sigma$  Ni-carbonyl anti-bonding orbital. There is also an increase in this excitation energy from 1.319 eV to 1.447 eV upon increasing the basis. The next excited state ( $2^1\Sigma^+$ ) carries the largest oscillator strength of the low-lying excited states considered, and shows only a small difference between the smaller and larger bases. This state can be qualitatively understood as a transition from the  $d_\sigma$  Ni-carbonyl bonding orbital to its anti-bonding counterpart (see figure 1).

Considering now the variation of the excited states along the LR-CC series we again see that the uncorrelated CCS is fortuitously close to CCSD, but overestimates by 0.1-0.7 eV. The transition strengths for the bright states are of the same orders of magnitude between CCS and CCSD, unlike Ni(CO)<sub>4</sub> above. The CCS excitation energies show less variation with basis than CCSD. The low cost doubles models fail spectacularly for Ni(CO) giving a negative excitation for the lowest  $1^1\Delta$  state, and CC2 also giving negative excitation energies for both other states while CIS(D) gives spuriously small excitation energies for those. CCR(3) shows an overestimation of excitation energies as in Ni(CO)<sub>4</sub>, although much less severe (maximum 0.6 eV). The CCR(3) excitation energies show less sensitivity to basis than CCSD. In both bases considered however the order of the  $1^1\Pi$  and  $2^1\Sigma^+$  states is inverted, although for both the states are within <0.2 eV of each other.

Again, similar to the saturated Ni(CO)<sub>4</sub>, TD-CAM-B3LYP performs very well here. For Ni(CO)<sub>4</sub> the ability of the functional to correctly describe the correct ground state is crucial. For TD-CAM-B3LYP there is no sensitivity to basis set observed. The oscillator strengths are the correct relative orders of magnitude although for the  $2^1\Sigma^+$  state it is consistently too large compared to LR-CCSD.

To further understand the electronic structure, and to possibly give insight as to why methods such as CC2 have such problems for these systems, CASSCF calculations were

performed to assess the nature of the electronic ground states of these systems. Using the (10,11) active space described above multiconfigurational calculations were performed on the ground state of both Ni(CO)<sub>4</sub> and Ni(CO) complexes and the contribution to the ground state by individual configurations analysed. It was found that electronic ground state in both cases was dominated by the configuration relating to a Ni 3d<sup>10</sup>4s<sup>0</sup>. However, the degree to which this configuration accounted for the total ground state was never more than 90%. For both Ni(CO) and Ni(CO)<sub>4</sub> it was found that the 3d<sup>10</sup>4s<sup>0</sup> electronic configuration accounts for around ~86% of the ground state with the next largest contribution (~10%) coming from the 3d<sup>8</sup>4s<sup>2</sup> configuration. Thus, there is a small but significant amount of multireference character that has consequences for the lower cost CC response methods.

While single reference methods describe the dominant ground state electronic configuration and geometric structure, the presence of the other configuration(s) means that the Hartree-Fock orbitals give rise to a partially multireference correlated wavefunction. The large T<sub>1</sub> amplitudes indicate a significant amount of orbital relaxation. Using a better set of underlying orbitals would give rise to a less multireference wavefunction. In the presence of an external field the orbital relaxation here is very large and the T<sub>1</sub> similarity transformed operators in CCn theory start cause problems. This effect is not generally seen in organic excitations and indeed CC2 has become the “go-to” method for charge-transfer excitations, while CC3 is the often the “gold-standard” in excited state benchmarking for small molecules. This type of feature has however recently started to be seen in transition metal containing systems in many complex cases including for example the permanganate ion MnO<sub>4</sub><sup>-</sup>, and TiO<sub>2</sub> clusters.

It is informative to compare the LR-CCSD results with those from NEVPT2 (table 4). Both methods agree well for the first dark 1 <sup>1</sup>Δ state but less well for the next, bright, 1 <sup>1</sup>Π state: 1.447 eV vs 2.540 eV. In fact the NEVPT2 excitation energy for this state is much closer to CCSDR(3) at 2.26 eV. MCCI (below) also shows this state around ~2.5 eV. Further higher order CC calculations such as EOM-CCSDT would be interesting to see if this state is one for which the very robust LR-(and EOM)-CCSD methods fair less well.

We finally investigate the electronic structure of the electronic states of Ni(CO) using MCCI<sup>47-49,52</sup> to calculate excited state energies, and a quantify their multireference character.<sup>56,57</sup> The cut-off (c<sub>min</sub>) for inclusion of configurations essentially determines the accuracy of a MCCI calculation and, in principle, MCCI can capture both static and dynamic correlation. We use c<sub>min</sub>=3x10<sup>-4</sup> and the both the cc-pVDZ and cc-pVTZ(D) bases, where the latter takes the standard cc-pVTZ basis but neglects f-functions on C and O, and g functions

on Ni, in conjunction 11 frozen orbitals. The full CI spaces for are of the order  $10^{21}$  and  $20^{23}$  Slater determinants for each basis respectively. The number of spin-adapted configuration state functions (CSFs) in the converged MCCI wavefunctions that approximate those full CI wavefunctions for each separate state are also given in Table 7. We note that MCCI further confirms that ground electronic state is a singlet, the lowest triplet being  $\sim 1.4$  eV above (in both bases). We see that increasing in basis has only a very modest effect on excitation energies ( $\sim 0.1$  eV), and a moderate increase in the size of the CI vectors. The MCCI excited state energies are always larger than those of LR-CCSD. This ties in with the CCR(3) excitation energies also being larger and the oscillatory convergence across the LR-CC series. The ordering of MCCI excited states agrees with both LR-CCSD and NEVPT2. The measure of multireference character (MR) shows that all singlet states (including the ground state) are of significant multireference character when expanded in Hartree-Fock orbitals. This is particularly true for the two bright states.

**Table 6a.** Lowest singlet electronic excited states (eV) of Ni(CO) with cc-pVDZ basis, oscillator strengths in parenthesis.

State	Character	CCS	CIS(D)	CC2	LR-CCSD	EOM-CCSD	CCR(3)	CAM-B3LYP
1 $^1\Delta$	$d\sigma^*$	1.572 (0.0000)	-1.352	-3.121 (0.0000)	0.765 (0.0000)	0.765 (0.0000)	1.367	0.991 (0.0000)
1 $^1\Pi$	$d\sigma^*$	1.610 (0.0003)	0.143	-5.603 (-0.2202)	1.319 (0.0004)	1.319 (0.0001)	2.260	1.594 (0.0003)
2 $^1\Sigma^+$	$\sigma\sigma^*$	1.169 (0.0121)	0.308	-2.504 (0.0000)	1.495 (0.0316)	1.495 (0.0368)	2.135	1.564 (0.0149)

**Table 6b.** Lowest singlet electronic excited states (eV) of Ni(CO) with cc-pVTZ basis, oscillator strengths in parenthesis.

State	Character	CCS	CIS(D)	CC2	LR-CCSD	EOM-CCSD	CCR(3)	CAM-B3LYP
1 $^1\Delta$	$d\sigma^*$	1.667 (0.0000)	-1.352	-2.681 (0.0000)	0.917 (0.0000)	0.917 (0.0000)	1.508	1.087 (0.0000)
1 $^1\Pi$	$d\sigma^*$	1.646 (0.0002)	0.143	-5.194 (-0.610)	1.447 (0.0001)	1.447 (0.0001)	2.378	1.668 (0.0003)
2 $^1\Sigma^+$	$\sigma\sigma^*$	1.217 (0.0119)	0.308	-2.336 (0.2228)	1.507 (0.0322)	1.507 (0.0322)	2.153	1.596 (0.0149)



**Table 7a.** Ni(CO) MCCI ( $c_{\min}=3\times 10^{-4}$ )/cc-pVDZ state energies relative to lowest totally symmetric singlet state, multireference MCCI diagnostic MR, and number of CSFs in converged CI solution.

State	Energy / eV	MR	CSFs
1 $^1\Sigma^+$	0.00	0.65	26320
1 $^1\Delta$	1.65	0.60	55309
1 $^1\Pi$	2.44	0.73	46962
2 $^1\Sigma^+$	2.54	0.68	56593
1 $^3\Delta$	1.41	0.43	45345
1 $^3\Pi$	2.10	0.54	50303

**Table 7b.** Ni(CO) MCCI ( $c_{\min}=3\times 10^{-4}$ )/cc-pVTZ(D) state energies relative to lowest totally symmetric singlet state, multireference MCCI diagnostic MR, and number of CSFs in converged CI solution.

State	Energy / eV	MR	CSFs
1 $^1\Sigma^+$	0.00	0.65	32489
1 $^1\Delta$	1.65	0.58	66207
1 $^1\Pi$	2.56	0.71	55764
2 $^1\Sigma^+$	2.69	0.67	67533
1 $^3\Delta$	1.45	0.43	60145
1 $^3\Pi$	2.56	0.71	55764

## Conclusions

We have applied a wide range of correlated excited electronic state methods to the saturated and unsaturated binary metal carbonyls Ni(CO)<sub>4</sub> and Ni(CO), including linear response and equation of motion coupled cluster theory, Monte Carlo configuration interaction (MCCI), complete-active space self-consistent field theory, multi-reference perturbation theories, and time-dependent density functional theory. For Ni(CO) we find that a correlated treatment is necessary to predict a closed-shell singlet ground state. For both we find that although they are qualitatively described by a simple single configuration (3d<sup>10</sup>) wavefunction there are some multi-reference effects associated with the 3d<sup>8</sup>4s<sup>2</sup> metal configuration that have very strong indirect effects on the performance of correlated excited state methodologies. CCn models fail due to the large T<sub>1</sub> amplitudes, although the full CC response (or equivalent EOM) approaches are very accurate in describing the excited states of these systems. MCCI further quantifies the significant multireference character of the ground and excited electronic singlet

states using a recently introduced metric. TD-CAM-B3LYP has an exceptional cost/performance for these very challenging electronic states. These metal carbonyls are simple yet display richness in their electronic structure that makes them excellent test cases for excited state quantum chemical methodologies.

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## TOC Graphic

