Chapter 7

Summary

The overall goal of this thesis was to investigate coherent control mechanisms on two organometallic complexes: $CH_3Co(CO)_4$ and $CpMn(CO)_3$. While for $CpMn(CO)_3$ the potential energy surfaces (PESs) and corresponding couplings are known from literature [40], all the electronic structure calculations for $CH_3Co(CO)_4$ have been performed from scratch. For each step along the process, the results from the quantum chemical and quantum dynamical calculations have been compared with those of the hydride analogue, $HCo(CO)_4$. The obtained dynamics for the hydride and methyl analogue are very different. The goal is to study the possible control of the competing ligand dissociation of R=H, CH_3 versus CO. Whereas in $HCo(CO)_4$ the hydrogen ligand dissociates very fast due to the different masses, in $CH_3Co(CO)_4$, the wavepacket dynamics on the two lowest-lying excited unbound states for the methyl complex indicate a simultaneous two bond breakage. The control of a single axial ligand dissociation was achieved using a pump-dump mechanism. The manganese complex was used as a model system for the development of nonresonant multiphoton transitions (NMT) and its application in optimal control theory (OCT). The theory has been successfully applied to a two-level system in which nonresonant two- and three-photon transitions have been investigated. The detailed summary is given below.

Quantum Chemistry   In section 6.1 a comparative study of two analogue organometallic molecules has been presented. The two molecules tetracarbonylhydridocobalt, $HCo(CO)_4$, and tetracarbonylmethylcobalt, $CH_3Co(CO)_4$, differ only in one of their axial ligands.

Due to the limited experimental information of the methyl complex, both molecules were optimized using DFT with the B3LYP functional. The experimental geometry for $HCo(CO)_4$ has been compared to the DFT optimized geometry. The DFT geometry agrees with the experimental bond lengths and angles. However, the lengths of the axial and equatorial cobalt-carbonyl bonds are reversed: the axial metal-carbon bond lengths are underestimated whereas the equatorial metal-carbon bond length is overestimated. Overall, the similarities of the experimental geometry for the hydrido complex with its optimized DFT geometry has validated the use of the DFT/B3LYP optimized geometry of the methyl complex for further calculations, and can be visualized in fig. 6.2.

The TD-DFT electronic spectrum for $HCo(CO)_4$ was investigated for the experimental geometry as well as for the DFT/B3LYP optimized geometry. The electronic spectrum for $CH_3Co(CO)_4$ was calculated at the same level of theory using the DFT/B3LYP optimized geometry. The CASSCF/MS-CASPT2 electronic energies were calculated and the electronic energies were compared, these energies are listed in table 6.1. Calculations from TD-DFT indicate an intercalation of two Metal-to-Ligand-Charge-Transfer (MLCT) states between the two low-lying Metal-to-Sigma-Bond-Charge-Transfer (MSBCT) states for the hydrido complex, and one state intercalated in the methyl complex. All transition energies from the ground state to all excited electronic states are minimized by more than 0.5 eV in comparison with the MS-CASPT2 calculations.

State correlation diagrams, shown in figs. 6.3 and 6.4, have been built for both complexes in which the two axial ligands were stretched 50Å from the cobalt center. Available bond dissociation energies were compared to experimental values as well as to other theoretical values. The MS-CASPT2 values differ significantly from those of CASSCF for all ligands except for the hydrogen, and tends to over-stabilize the system. This discrepancy has been attributed to the unbalanced orbital description between the equilibrium and the asymptotic regions.

The electronic singlet and triplet states were correlated for $HCo(CO)_3$ and $CH_3Co(CO)_4$ as the first step in calculating the 2-D PESs. For the hydrido complex the five lowest-lying electronic states for the A$'$ symmetry were correlated and the three lowest-lying electronic states for the methyl complex were correlated. The 2-D PESs for the first five low-lying electronic states of both complexes were built. The 1-D cuts of the PESs for both complexes are presented in fig. 6.5. The 2-D PESs of the two MLCT states of the methyl complex lying highest in energy, were built between 1.78 and 2.69 Å and 1.71 and

2.41 Å for the q_1 and q_2 coordinates corresponding to the Co-CH$_3$ and the Co-CO bond stretches.

Using the FGH method, the first twelve vibrational eigenfunctions were calculated for CH$_3$Co(CO)$_3$ and HCo(CO)$_3$ within the 2-D model for the electronic ground state and are plotted in figs. 6.8 and 6.7, respectively. The fundamental vibrational frequencies for each coordinate were compared to the limited experimental data as well to corresponding harmonic DFT/B3LYP frequencies and are listed in table 6.6. The experimental stretching vibrational mode for the hydrogen atom is comparable to the calculated value, which is $\sim$ 200 cm^{-1} lower in energy. Vibrational frequencies obtained from anharmonic PESs have been compared to the frequencies obtained from a full harmonic DFT calculation. The corresponding vibrational modes of the two calculations are within 100 cm^{-1}, indicating that the 2-D PESs are in reasonable agreement around the minimum, where a harmonic description is valid.

Quantum Dynamics   The theoretical absorption spectra for both cobalt complexes have been calculated and are presented in fig. 6.9. The autocorrelation functions for the two MSBCT unbound states quickly decay to zero and do not contribute to the absorption spectra. The inherent structure of the two MLCT bound states cause revivals in the auto-correlation function and produce two sets of peaks corresponding to each of these states. Only the peaks corresponding to the c^{1}E state for the methyl complex are irregular and result from the complex wavepacket dynamics. The peaks corresponding to the b^{1}A$_1$ state show a regularity that corresponds to a rather pure Co-CO stretching vibrational frequency. The methyl complex's absorption spectrum is also composed of two sets of peaks. The peak spacings are regular and correspond again to a nearly pure Co-CO stretching vibration.

From the wavepacket dynamics for CH$_3$Co(CO)$_4$ that were initiated from a delta pulse and multiplied by a constant transition dipole function, it was found that the wavepacket motion on the b^{1}A$_1$ state corresponds to a substantial Co-CO bond elongation, with little elongation of the Co-CH$_3$ bond. At the same time, the wavepacket evolution on the two unbound a^{1}E and b^{1}E states indicates a simultaneous breakage of both metal-ligand bonds, and snapshots of the evolution on the a^{1}E are shown in fig. 6.11. These simulations were done by neglecting the diabatic couplings.

Quantum Control   An extension of the Tannor-Rice control scheme has been success-
fully applied to control the two-bond breakage of the methyl complex, incorporating the
ground a^1A_1 state, and the excited electronic states a^1E and the b^1A_1. A new control quan-
tifier, the angle of dissociation, is used to measure the extent of control that is achieved.
Per definition, if the angle of dissociation is $90°$ a complete dissociation of the Co-CO
bond is achieved, leaving the rest of the molecule intact. If the angle of dissociation is $0°$,
then the Co-CH$_3$ bond is exclusively broken. Based on a series of simulations in which
the delay time between the pump and the dump pulse is varied, the angle of dissociation
was calculated. The maximum angle of dissociation obtained was $32.9°$ and the mini-
mum angle obtained was $-0.2°$. Snapshots of the wavepacket's temporal evolution are
given in figs. 6.17 and 6.18. Both of these values have been compared to the natural angle
of dissociation, i.e. the angle of dissociation occurring upon a delta-pulse excitation, of
$27.4°$. The single breakage of the Co-CH$_3$ bond has been achieved. Again the simulations
were done using the Franck-Condon approximation and the diabatic couplings have been
neglected.

NMT and its Application to OCT   The theory of NMT has been presented in chap-
ter 5 by solving the effective time-dependent Schrödinger equation [120, 121]. Because
the complete space for polyatomic molecules can not be calculated, the space has been
partitioned into primary and secondary spaces, corresponding to those states which are
calculable and those that are not, respectively. Because the complete space is partitioned
and corresponding projection operators are employed, the exact expressions depicting
NMT become nonlocal in time. To remove this behavior, the rotating wave approxima-
tion has been introduced along with the density of states for the secondary states, and it
has been assumed that the kernel is expandable in powers of the field Hamiltonian de-
fined in secondary state space. The effective dipole matrix elements are taken as constant
functions, i.e. in the Franck-Condon approximation, and transition dipole matrix element
into the secondary state space are parameterized. All simulations have neglected diabatic
couplings.

Transitions induced by nonresonant multiphoton excitations are simulated via their cor-
responding equations of motion within a two-level system, and are presented in sec-
tion 5.4.2. Comparison of the population induced by a nonresonant two-photon transition
with that induced by an off-resonant one-photon transition has been made, see fig. 6.20.
The same has been done for nonresonant three-photon transitions, and are presented in

fig. 6.21. Although the single-photon excitation transfers a similar amount of population from the ground state to the excited state over the first half of the laser pulse, the second half reduces this transient population to nearly zero. The difference in population between the single-photon and the two- or three-photon transitions, upon termination of the laser pulse, is larger in magnitude for the two-photon than for the three-photon transitions, as was expected. Population analysis has also been performed with varying effective dipole moments and density of secondary states. The population intensities were as expected and are shown in fig. 6.22.

The theory of NMT has been implemented into the standard approach to OCT, for the non-resonant two- and three-photon transitions for a two-level system. The resonant single-photon transitions were used for comparison. In all three cases the yield of the target state is maximized with the constraint placed on the field strength via the penalty factor. Convergence occurred between 10 and 15 iterations, see fig. 6.23, indicating the successful implementation of NMT into OCT. Subsequent studies were performed for the nonresonant two-photon transitions. The first study varied the penalty factor in order to control the field strength of the laser field. For large control yields, nonresonant transitions tend to occur in the strong-field regime, optimizing both the amplitude and the position of the propagated wave function and the results are given in table 6.7. The renormalized control yield is used to measure the probability that the wavepacket has moved to the position of the target, effectively neglecting the amplitude. Limiting the control field to lower field strengths by increasing the penalty factor produces lower control yields, but altered only minimally the renormalized control yield, indicating that the position of the target state was reached. The second study investigated the effect of changing the target state. For all target states investigated, OCT converged and the control field, control yield, and renormalized control yield were recorded in table 6.8. In the two-level system the investigation of NMT and its application to OCT have been successfully applied. For each target state investigated a control field was found which optimized it by maximizing the overlap between the target and the final wavepacket with a penalty contraint on the field strength. This indicates the applicability of the NMT theory into OCT which can be used to develop further optimal laser pulses for control experiments.

In conclusion, the playground (i.e. the PESs) for wavepacket dynamics has been built and the dynamics of nuclear wavepackets have been analyzed. Quantum control of ligand dissociation has been attained and the theory of nonresonant transitions has been presented and successfully implemented into optimal control theory.

Outlook The methyl complex was successfully controlled for the exclusive single bond breakage of the Co-CH$_3$ bond. A control mechanism for the Co-CO bond remains a challenge. It could be attainable, e.g. if the two MLCT states were correlated to further internuclear distances and the states crossing with them were included as new possible control routes. Another point of interest is to include more degrees of freedom, such that the axial ligands can be investigated. Furthermore, the control mechanisms elucidated theoretically could be proposed to experimentalists for verification.

The presented NMT theory and its application to OCT should be expanded to include sequential nonresonant two- and three- photon transitions for the CpMn(CO)$_3$ complex. The inclusion of the sequential process will allow for a better emulation of the experimental feedback-loop control experiments, as that presented in ref. [27]. In addition, a refined model should include a more accurate description of the effective transition dipole moments. The optimization of a target state on 2-D PESs could also be investigated with the developed NMT theory. Since many processes occur via NMT, the theory could be applied to several systems and the optimized control fields could be produced. These fields could then be either transferred for experimental use or compared with the optimized feedback-loop control fields. Furthermore consideration of more degrees of freedom along with diabatic effects could be studied.