Chapter 5

Conclusions and outlook

The ultimate goal of this work has been the simulation and interpretation of pump-probe and control experiments involving the the ultrafast cleavage of the Mn-CO bond in $CpMn(CO)_3$ [129].

For this purpose, state-of-the-art *ab initio* MR-CCI/CASSCF potential energy curves have been calculated for the low-lying neutral singlet and doublet ionic states along the Mn-CO coordinate of $CpMn(CO)_3$. The influence of triplet states should be negligible and IVR should not have a strong influence since the loss of the first CO takes place in less than 200 fs. At the low temperatures at which the pump probe and control experiments have been performed (below 10 K), the molecule should prefer a staggered conformation of the $Mn(CO)_3$ group with respect to the cyclopentadienyl (Cp) ring. In contrast, at room temperature, it rotates freely. Therefore, we have simulated the Mn-CO dissociation of the Mn-CO bond lying in the symmetry plane of the staggered molecule with C_S symmetry. With an error of approximately 0.2-0.3 eV, the experimental and theoretical (vertical) excitation energies agree rather well (see discussion in sections 3.3 and the comparison of the theoretical and experimental absorption spectrum in section 4.2, figure 4.7).

The kinetic couplings have been calculated approximately using the leading CI (*cf* figures B.1-B.4 and figures B.18-B.19) and MO coefficients (*cf* figure B.5) of the MR-CCI wave function. The b^1A'-c^1A' and a^1A''-b^1A'' kinetic coupling terms are shown in figures 3.8, 3.11, 3.10 and 3.12. All other kinetic coupling terms are given in appendix B. With the experimental photon energies, only the lowest neutral excited singlet states, b^1A', c^1A', a^1A'' and b^1A'', are populated. These neutral excited states, the electronic ground state a^1A', and the ionic doublet states $(a^1A'')^+$, $(a^1A')^+$ and $(b^1A')^+$ have been included in our theoretical simulations of the pump-probe and control experiments. The *ab initio* transition dipole moments for transitions betweeen the ground and the excited electronic states are depicted in figure 3.4 and those for transfers from the excited to the ionic states have been approximated using the CI coefficients (*cf* figures 3.15, 3.16, 3.17 and 3.18)

Wave packet propagations both in the adiabatic and the diabatic representations have shown that the coupling between the a^1A'' and b^1A'' states has a strong influence on the photodissociation dynamics whereas the b^1A'-c^1A' coupling is negligible. The adiabatic and the diabatic picture are equivalent and are connected via a unitary transformation. In our theoretical simulations of the absorption, the pump-probe, and the control experiments, the adiabatic representation has been employed. Simulations on the uncoupled b^1A' and c^1A' states using δ-pulses to calculate a dissociation probability confirm an ultrafast ($\approx$ 100 fs) loss of the first CO ligand in experiment (*cf* figure 4.10).

Two mechanisms have been proposed: one of them describes the pump-probe experiment; the other one reveals how the optimal control pulse produces predominantly the parent ion $(CpMn(CO)_3)^+$.

The mechanism that describes the pump-probe spectra of the parent, $(CpMnCO_3)^+$, and the daughter, $(CpMnCO_2)^+$, ions mainly relies on the excitation of the bound b^1A'' state (pump); the repulsive a^1A'' is populated by means of the a^1A''-b^1A'' kinetic coupling (*cf* figure 4.26). The chosen probe pulse transfers simultaneously population from the b^1A'' neutral to the $(b^1A')^+$ ionic state producing the parent ion and from the a^1A'' neutral to the $(a^1A'')^+$ ionic state yielding the daughter ion. Oscillations with a period of 80 fs in theory and 85 fs in experiment are superimposed on the fast decaying pump-probe signal (see figure 4.23). The decay time due to a^1A''-b^1A'' internal conversion is 166 fs (*cf* figure 4.25).

The control pulse optimizing the parent ion yield must avoid population of the b^1A'' state (which would decay to the daughter via the nonadiabatically coupled a^1A'' state) and should instead predominantly excite the bound c^1A' state, not coupled to any other state. This requires higher pump energies in the control simulation than in the pump-probe simulation (analysis). The probe should be resonant to an ionic state slightly before the c^1A' state wave packet reaches the c^1A' potential barrier at which part of its population decays by dissociation to neutral fragments. An optimal delay time of 85 fs between the pump and the probe pulse has been found in accord with experiment (*cf* figure 4.29).

Alternative ways of producing the parent and the daughter ion via an excitation to the b^1A' state have been discussed in section 4.5.1. On the one hand, pump and probe energies of 3.23 eV and 3.92 eV, respectively, mainly produce the parent ion (*cf* figure 4.18). On the other hand, the same pump and a higher probe energy (> 5 eV) will predominantly yield the daughter ion.

In the future, the "inversion" of the experimental pump-probe and control data, *i.e.* the shift of the ground state minimum (0.04 Å) and the scaling of the the kinetic couplings ($\times$ 0.75), may be extented to fix other parameters such as vertical

excitation energies.

The influence of the coupling to other degrees of freedom, especially the other two out-of plane Mn-CO stretchings should not be severe, but a three-dimensional study should be performed in order to check and to exclude the possibility of the simultaneous loss of two CO ligands. A study of the consecutive loss of all ligands, including the Cp ring, is beyond the capabilities of the applied *ab initio* quantum chemical and dynamical methods (at least with current computer capabilities). An alternative analysis of competing preparations of product ions via laser excitations of organo-metallics, which assumes statistical redistribution of the available energy in all vibrational and rotational degrees of freedom might be a solution [36]. However, the latter approach has not been extended to optimal control.

Similar discoveries of the mechanisms of optimal control should be possible for other systems having two important properties, found in the present system. First, the target should be produced by few, preferably just two main sequential processes *e.g.* excitation or photodissociation followed by ionization. Each of them should employ a small number of photons, avoiding significant Stark-shifts. Second, it should be possible to select the target channel while suppressing the competing ones, by means of well-placed sub-pulses with slightly different frequencies within the band width of the reference pulse. This requirement points to systems with a sufficiently large density of electronic excited and ion states leading to the target or competing channels.