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Analysis and control of ultrafast photodissociation processes in organometallic molecules

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Abstract. In this paper we characterize the ultrafast fragmentation in electronically excited $Fe(CO)_2(NO)_2$ and $CpMn(CO)_3$ by means of femtosecond time-resolved spectroscopy combined with mass spectrometry. From the transient two-color multi-photon ionization data, it was possible to record the transients of the parent molecule ions and their photofragment ions. The experimentally observed decay times indicated an ultrafast loss of the first ligands (sub-100 fs decay times). Further we performed a feedback control experiment on the photofragmenting $CpMn(CO)_3$ molecular system in order to maximize the yield of desired ionic products through pulse modulation. The shape of the pulses obtained from optimization reflect well the intrinsic molecular dynamics during photofragmentation and the change of the $CpMn(CO)^+/CpMn(CO)_3^+$ ratio shows a clear evidence for the capability of the optimization method to find tailor-made system-specific pulses.

PACS. 82.53.Eb Pump probe studies of photodissociation – 31.70.Hq Time-dependent phenomena: excitation and relaxation processes, and reaction rates – 82.50.-m Photochemistry – 82.50.Nd Control of photochemical reactions – 82.53.-k Femtochemistry

1 Introduction

Organometallic compounds containing CO or NO ligands are good model systems for investigating unimolecular photofragmentation channels. The chromophoric character of the metallic core allows to excite these molecules into different electronic states. After the electronical excitation a fast energy redistribution and loss of ligands can be observed [1]. The time evolution of the system can be monitored by means of pump-probe spectroscopy. In the past, such systematic investigations were performed, for example, by Zewail *et al.* [2], Banarez *et al.* [3] and Trushin *et al.* [4]. The observed transient ionic fragmentation patterns indicated an ultrafast loss of the CO ligands and the involvement of different intermediate states (different locations on the potential energy surfaces) in the process of photodissociation. These particular properties make carbonyl-containing compounds good candidates for controlling their molecular dynamics in real time by means of pulse shaping techniques [5] - based on Rabitz' proposition to employ self-learning feedback algorithms [6] to drive the reaction dynamics along a desired path. The first important experimental step in this regard was performed by Gerber *et al.* [7] who optimized a femtosecond laser pulse profile which then controlled the parent ion or a fragment ion yield in the fragmenting metal-carbonyls, *e.g.* $CpFe(CO)_2Cl$. The possibility to use optimal laser pulses for the control of organometallics has been demonstrated by model calculations, for example by Manz *et al.* [8]. In order to choose the proper molecular systems and to draw a consistent picture between the time scales of the observed process and the information content which may be extracted from the optimized laser fields, first we have performed systematic pump-probe experiments on $Fe(CO)_2(NO)_2$ and $CpMn(CO)_3$ ($Cp = \eta^5$-C_5H_5). In the next stage, we performed feedback loop experiments on the system $CpMn(CO)_3$.

2 Experimental setup

The laser system consisted of a Spectra Physics 3960 Tsunami Ti:Sa femtosecond laser, which was pumped by a Spectra Physics Millenia V Nd:YLF laser and produced seed pulses of about 70 fs duration centered at 800 nm for the Quantronix regenerative multipass amplifier. The amplifier produced pulses of about 90 fs duration and 1.5 mJ energy at 1 kHz repetition rate. The laser pulses were analyzed with a Jobin-Yvon spectrometer and a SHG FROG (Polytec Femtos). In the pump-probe experiment the light pulses were split up into a pump and a probe beam. The pump pulse was frequency doubled and the probe pulse passed through a variable delay. The molecular beam was produced in an adiabatic beam expansion apparatus by coexpansion of the probe vapor with argon carrier gas across a nozzle of 70-80 μm diameter into the

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vacuum. The molecular beam passed between the electrical lenses of a Balzers QMG 420 quadrupole mass spectrometer, which was perpendicularly oriented both to the cluster beam and to the irradiated laser beams in order to extract the emerging photoions. In the optimization experiment, a single laser beam (with wavelength centered at 800 nm) passed through a pulse shaper setup, which allowed a simultaneous phase- and amplitude modulation of the laser pulses by applying voltages to a liquid crystal spatial light modulator (SLM) consisting of 2×128 pixels [5]. By computer control, pulses of arbitrary form, like linearly chirped pulses, pulse trains etc. could be produced. These shaped pulses were then focussed on the molecular beam and the current of the desired mass-selected product photoion was taken as feedback signal for the optimization algorithm. The optimization algorithm altered the pulse shaper settings in order to maximize the desired ion signal. We applied an algorithm based on evolutionary strategies [9,10].The optimization setup and the algorithm is described in details elsewhere [11].

3 Experimental results and discussion

The first experiments performed on $CpMn(CO)_3$ with laser light centered at 400 nm showed very efficient saturation of the ion signal at even very small laser intensities, indicating a resonant step in the sequential multi-photon ionization process. In order to avoid saturation, we employed pump pulses of 10 μJ energy centered at 400 nm and probe pulses of 30 μJ energy centered at 800 nm. Fig. 1 shows a set of the pump-probe spectra recorded for the parent molecular ion $CpMn(CO)_3^+$ and its fragment ions $CpMn(CO)_2^+$, $CpMn(CO)^+$ and $CpMn^+$. In order to get the corresponding decay times, a deconvolution algorithm was used in the data analysis. The resulting decay times and the time shift of the transient signal maximum for the $CpMn(CO)_3$ system are contained in Tab. 1. The transients of the $Fe(CO)_2(NO)_2$ system (parent ions and photofragment ions) were recorded and analysed by employing 400 nm pump and 800 nm probe laser wavelength and the results of the data analysis are summarized in Tab. 2. The fast decay times and the progressive shift of the time-resolved ion signal maximum observed in both molecular systems indicates a possible consecutive population of several intermediate states involved in the investigated multi-photon fragmentation and ionization process leading to the formation of individual ions.

Table 1. $CpMn(CO)_3$ system: Peak shift and decay times obtained from the transients.

Transient ion signal	Peak shift Δt/fs	Decay time τ_{decay}/fs
$CpMn(CO)_3^+$	0	66
$CpMn(CO)_2^+$	55	90
$CpMn(CO)^+$	75	180
$CpMn^+$	90	220

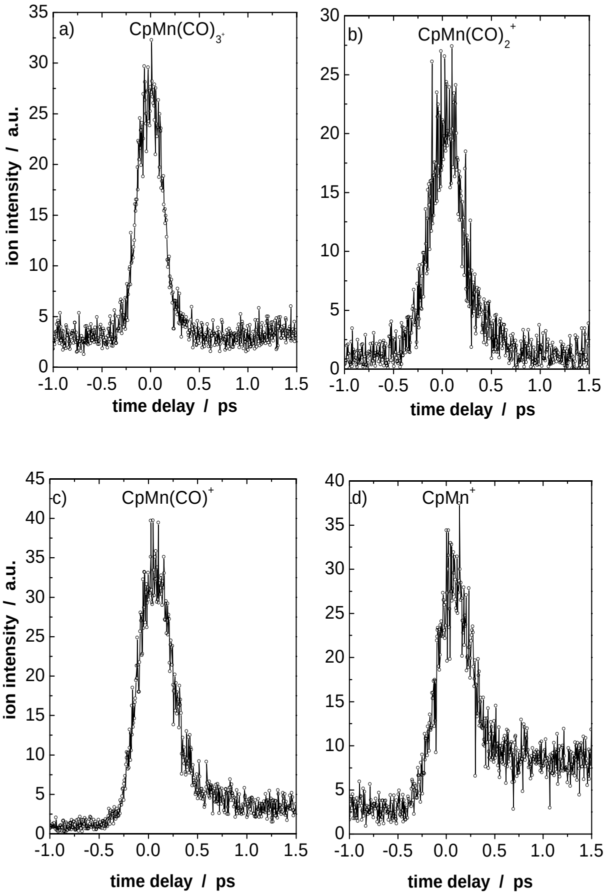

Fig. 1. Set of transient ion signals recorded on the $CpMn(CO)_3$ system.

Table 2. $Fe(CO)_2(NO)_2$ system: Peak shift and decay times obtained from the transients.

Transient ion signal	Peak shift Δt/fs	Decay time τ_{decay}/fs
$Fe(CO)_2(NO)_2^+$	0	20
$Fe(CO)(NO)_2^+$	0-10	70
$Fe(NO)_2^+$	20	180
$Fe(CO)_2(NO)^+$	30	220
$Fe(CO)(NO)^+$	50-70	200
$Fe(CO)_2^+$	90	180
$Fe(NO)^+$	110	70
$Fe(CO)^+$	130	510

The first theoretical calculations show that in the case of $CpMn(CO)_3$ there are two crossing states present in the used excitation energy region [12]. The calculated time of the departure of the first CO ligand ~ 63 fs is in a good agreement with the experimental observations. Taking the laser pulse duration and the somewhat slower dynamics observed in the pump-probe spectra of the $CpMn(CO)_3$ system, this system has been chosen for the first optimization experiment to control the ion yield of different

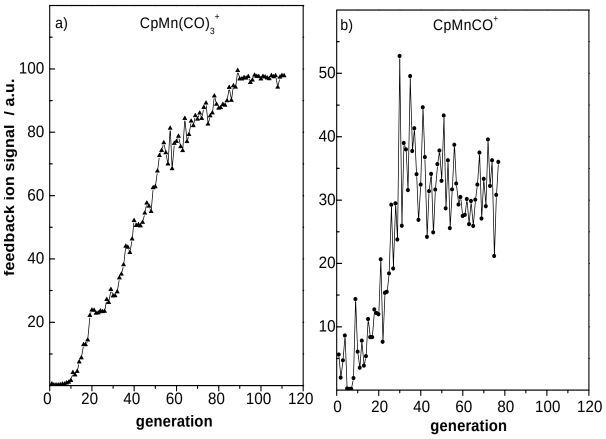

Fig. 2. Evolution of the ion yield during the optimization experiment plotted for the CpMn(CO)$_3^+$ signal (a) and the CpMn(CO)$^+$ signal (b).

Table 3. CpMn(CO)$^+$:CpMn(CO)$_3^+$ mass peak ratio obtained from the optimization experiments.

Pulse form	CpMnCO$^+$:CpMn(CO)$_3^+$ mass peak ratio
optimized for CpMn(CO)$_3^+$	1:16
reference pulse (no chirp)	1:13
optimized for CpMn(CO)$^+$	1:6

photoproducts. In order to avoid laser intensity effects, only the phase of the laser pulse was optimized in the experiment. The evolution of the ion yields of CpMn(CO)$_3^+$ and CpMn(CO)$^+$ during the optimization procedure (Figs. 2a and 2b) and the comparison of the resulting ion yields from the mass spectra (Tab. 3) indicate, that the control experiment lead to a substantial increase of the desired ion yield with respect to the other ion. The ratio of the CpMn(CO)$^+$/CpMn(CO)$_3^+$ ion yield changed by approximately 150%. The FROG traces of the optimized pulse forms are shown in Figs. 3a and 3b, the retrieved pulse forms are shown in Figs. 4a and 4b. The pulse sequence acquired for the maximum CpMn(CO)$_3^+$ ion yield consist of three pulses of 36-40 fs duration. The effective duration of the leading double pulse is approximately 100 fs, similar to the duration of the initial unchirped laser pulse (90 fs) centered at 800 nm. The pulse form can be explained by considering a 2-photonic excitation process and a subsequent 3-4-photonic ionization step together with the fast 66 fs decay of the CpMn(CO)$_3^+$ signal. The third pulse of small intensity very likely represents a second ionization pulse ionizing a fraction of excited parent molecules which were later excited with the second pulse. In the case of the CpMn(CO)$^+$ fragment ion, the pulse train consists of a double pulse. The first pulse acts as a pump pulse exciting the CpMn(CO)$_3$ molecule. The second pulse (ionization) arrives approximately 80 fs after the first pulse (effective pulse length of this double pulse is about 145 fs). The second pulse ionizes the actual (in this case maximal) population of the involved state(s) of neutral CpMn(CO) which gives rise to a maximum CpMn(CO)$^+$ fragment ion signal. The timing of the second pulse corresponds very well to the peak shift of the CpMn(CO)$^+$ transient pump-probe signals with respect to the excitation step.

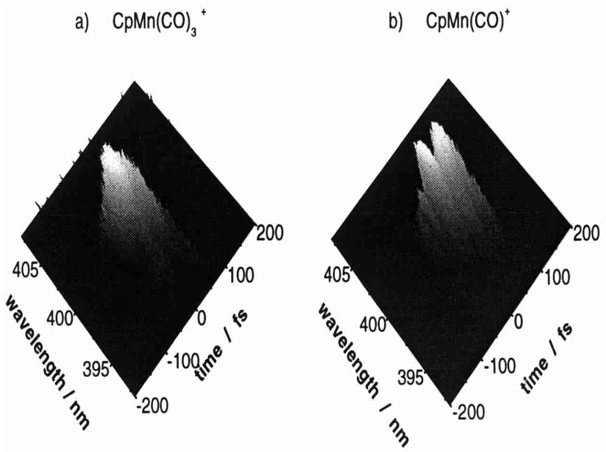

Fig. 3. SHG FROG traces of the optimized pulses acquired from the optimization experiment for CpMn(CO)$_3^+$ (a) and CpMn(CO)$^+$ (b).

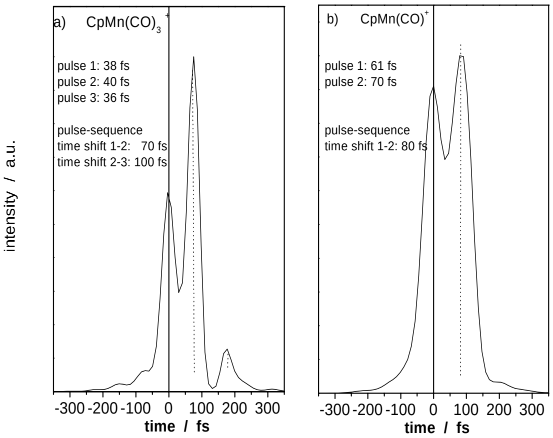

Fig. 4. Optimized pulse shapes acquired from the FROG analysis for CpMn(CO)$_3^+$ (a) and the CpMn(CO)$^+$ (b).

4 Conclusion

From the two-color pump-probe data we have characterized the ultrafast molecular dynamics of CpMn(CO)$_3$ and Fe(CO)$_2$(NO)$_2$ molecules, electronically excited by a sub-100 fs laser pulse. The loss of the first CO ligand from CpMn(CO)$_3$ seems to take less than 100 fs according to theory and experiment. The peak shift of the transient ion signal provides clear evidence for sequential population of the intermediate states involved in this process.

Under given experimental conditions, no signal indicative of an oscillatory wave-packet in excited $CpMn(CO)_3$ was resolved in the spectra. Furthermore, we have performed a feedback optimized control experiment on this photofragmenting system. The experiment controlled the yield of certain ions, implying the control of populations of the corresponding neutral molecular state(s). The acquired optimized laser pulse trains well reflected the intrinsic properties of the consecutive population of states observed in the time resolved experiment. Currently, a new optimization experiment on the $Fe(CO)_2(NO)_2$ system with sub-50 fs laser pulses is under preparation.

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