Ultrafast Photodissociation Dynamics of Isolated Ironpentacarbonyl

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Introduction

The photochemistry of metal carbonyls has received a wealth of interest in the last decades [1]. Metal carbonyls are important photocatalysts of many organic reactions [2]. Therefore, it has become important in recent years to understand the mechanisms by which these complex molecules photodissociate loosing one or several CO groups.

$Fe(CO)_5$ is a prototype molecule whose study can provide a good understanding of the photodissociation mechanisms of metal carbonyls. For this molecule, concerning its molecular and electronic structure, plenty of experimental and theoretical information is available (see Refs. in [3,4]).

The energetics of this molecule is presented in Fig. 1. The absorption spectrum is rather structureless and exhibits a strong band centered at about 50,000 cm^{-1} with a shoulder at 41,600 cm^{-1} (indicated by arrows in the figure). These two bands have been assigned to metal to ligand charge-transfer (MLCT) $d \rightarrow \pi^*$ transitions.

From the experimental point of view, many studies have been reported on the photodissociation of $Fe(CO)_5$ in the gas phase using nanosecond lasers in combination with other techniques (see Refs. in [3,4]). In all experiments, where multiphoton ionization (MPI) with nanosecond lasers was applied, the main photodissociation product was Fe^+, but in none of these experiments, the parent $Fe(CO)_5^+$ ions have been observed. It has been a subject of controversy, whether the loss of ligands by the metal atom after laser excitation occurs stepwise or in a concerted way.

Several theoretical calculations suggested mechanisms for the photodissociation and gave estimates for the involved time scales. Recent theoretical studies by Daniel *et al.* on metal carbonyl hydrides [5,6] have proposed that the time scale for the cleavage of the metal-CO bond is as short as 100 fs.

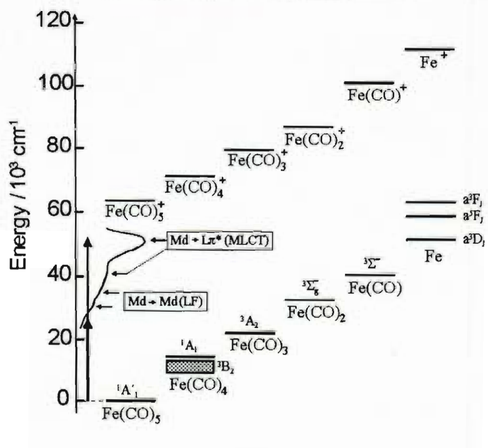

Figure 1 Energetics of $Fe(CO)_5$ and excitation scheme

Since no technique applied thus far has been fast enough to measure the primary photodissociation of $Fe(CO)_5$ in real time, the application of femtosecond laser studies is very timely. The femtosecond time scale is the ultimate time scale for the nuclear motion in molecules. Femtosecond techniques are therefore an ideal tool for real-time observations and control of chemical reactions[7].
The first femtosecond time resolved gas phase experiment on metal carbonyls was recently reported by Zewail and coworkers [8]. In that cornerstone experiment, they studied the ultrafast fragmentation dynamics of $Mn_2(CO)_{10}$.
We report on experiments where the photodissociation dynamics of $Fe(CO)_5$ in a molecular beam has been studied with femtosecond time resolution . The parent molecule and all the fragments were detected after femtosecond laser ionization in a linear time-of-flight (TOF) spectrometer. Transient ionization spectra of the parent molecule and of every fragment were measured by using the femtosecond pump-probe technique. From the results obtained, it can be concluded that the photodissociation of $Fe(CO)_5$ up to Fe(CO) occurs in about 100 fs. The subsequent dissociation of Fe(CO) into Fe + CO occurs on a longer time scale of 230 fs [3,4].

Experimental Setup

The experimental setup has been described in detail elsewhere [9] and only a brief description will be given here. An amplified Ti:Sapphire laser system yields pulsed femtosecond laser radiation centered at 800 nm with a duration of 70 fs and a pulse energy of 1mJ at a repetition rate of 1 kHz. After second harmonic generation, the 400 nm and 800 nm radiation is separated by means of a dichroic mirror into two beams. The pump laser pulses (400 nm) are delayed with respect to the probe laser pulses (800 nm) using a computer controlled Michelson-type interferometer. Both laser beams, appropriately attenuated, are recombined using a dichroic mirror and focused into the molecular beam chamber.
The molecular beam apparatus consists of two differentially pumped chambers one of them containing the $Fe(CO)_5$ molecular beam source and the other one a linear time-of-flight (TOF) spectrometer with a microchannel plate (MCP) detector. The $Fe(CO)_5$ sample, used without further purification (98%; Stream Chemicals), is taken directly from the cylinder at room temperature (vapor pressure of $\approx 3 \cdot 10^3$ Pa) and expanded through a nozzle of 50 μm into high vacuum (10^{-5} Pa).
The transient ionization spectra, *i.e.* the ion signal for a given mass in the TOF spectra dependent upon the time delay between the pump and the probe lasers, are measured by means of boxcar integrators. The transients were fitted using a non-linear least square method based on a Marquardt-Levenberg algorithm where the corresponding molecular response function (single or multiple-exponential with rise and decay components) was convoluted with a gaussian whose full-width-half-maximum (FWHM) corresponds to the cross-correlation of the pump and probe laser pulses.

Results and Discussion

Nanosecond and femtosecond multiphoton ionization-TOF spectra

Figure 2 shows time-of-flight (TOF) spectra obtained by MPI with nanosecond (ns) and femtosecond (fs) laser pulses. When using nanosecond laser pulses (337 nm, $\approx 10^9$ Wcm^{-2}), the only mass peak observed in the TOF spectra is the final photoproduct Fe^+. No evidence of larger fragment ions $Fe(CO)^+_{4-1}$, or the parent ion $Fe(CO)^+_5$ was found which is in agreement with earlier nanosecond laser studies (see Refs. in [3,4]). $Fe(CO)_5$ absorbs a photon already within the rising edge of the laser pulse and the molecule dissociates. The resulting fragment molecules absorb additional photons of the same laser pulse and can dissociate further. The ultimate photoproduct is Fe^+.

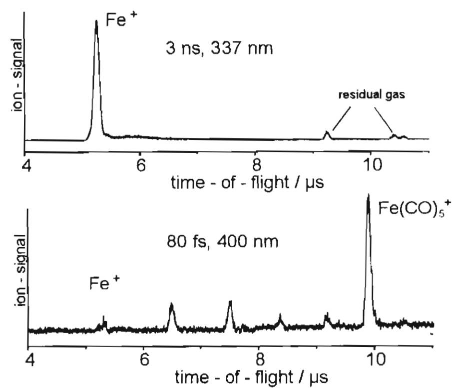

Figure 2 Comparison of TOF spectra obtained by MPI with ns laser (upper part) and fs laser (lower part).

The use of femtosecond laser pulses leads to a completely different picture. Mainly the parent ion $Fe(CO)^+_5$ appears in the fs-TOF spectrum obtained at 400 nm ($\approx 5 \cdot 10^{12}$ Wcm^{-2}). Ladder switching, as observed with ns laser excaitation is efficiently supressed. For laser intensities exceeding $\approx 5 \cdot 10^{13}$ Wcm^{-2} all the fragment ions $Fe(CO)^+_{4-0}$ and even CO^+ start to appear. Increasing of the pulse durations from 80 fs to 100 ps enlarges the amount of fragmentation. For laser pulswidths of more than 70 ps, Fe^+ is the only ion observed. These observations already show that the photodissociation of $Fe(CO)_5$ is ultrafast and one has to use ultrashort laserpulses to examine the fragmentation dynamics of this molecule in detail. The fragmentation pattern strongly depends on the fs-laser wavelength, the intensity and the pulse duration, which is discussed in detail in [4].

Transient ionization spectra

One and two color pump-probe experiments were performed using the fundamental wavelength (800 nm) and the second harmonic (400 nm) of the Ti:Sapphire femtosecond laser system. The 400 nm (pump) laser pulse excites $Fe(CO)_5$ by two photon excitation to the MLCT band (see Figure 1) and the molecules start to dissociate. After a variable delay time, the 800 nm (probe) laser pulse takes a snapshot of the evolving system. The probe laser produced ions are detected by a TOF mass spectrometer. The transient for a given mass is the ion signal *vs.* delay time.

Figure 3 shows the measured transients of the parent molecule and of every fragment. For positive delay times, the 400 nm laser was the pump and the 800 nm was the probe. All the transients were measured with attenuated pump and probe laser beams, where each of the lasers alone produces a negligible amount of ions. Under these experimental conditions, the observed dynamics has to occur in the neutral molecule where the probe laser induces the ionization.

The ion signal before time zero, when pump (400 nm) and probe (800 nm) lasers interchange their role, will not be discussed here. In the following, that part of the transients is analyzed for which the 400 nm pulse excites the molecule and the subsequent dynamics is probed by 800 nm photons.

All the measured transients were fitted to single or multiple-exponentials with rise and decay times taking into account the pump and probe laser pulse durations as indicated in the experimental section. The results of the fits for the parent molecule and all fragments are shown in Figure 3 as solid lines. The transients of the parent and the fragments $Fe(CO)_{4,3,2}$ were fitted to single exponentials with decay times of 100±5 fs, 105±5 fs, 115±5 fs and 150±20 fs, respectively. Note that $Fe(CO)_{4,3,2}$ transients show time shifts of 20±5 fs, 30±5 fs and 60±15 fs respectively, with respect to the maximum of the $Fe(CO)_5$ signal. The Fe(CO) ionization transient shows a slower rise than that of the cross correlation of the pump and probe laser, and was fitted with a rise time of 120±20 fs and a longer decay time of 230±20 fs. The transient of the atomic Fe fragment was fitted to a single-exponential rise with a time constant of 260±20 fs, and a longer decay time of 490±50 fs.

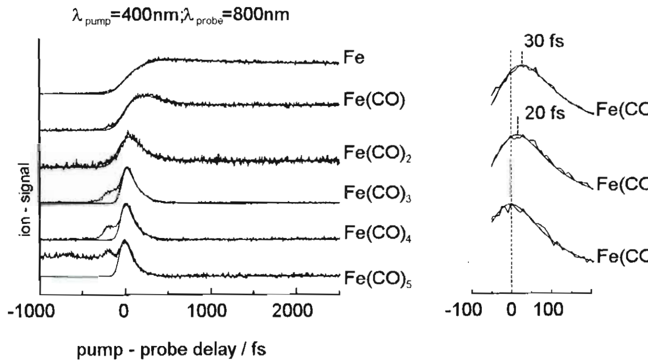

Figure 3 Two color (400 nm / 800 nm) femtosecond transient ionization spectra of $Fe(CO)_5$ and of the fragments. The solid lines represent fits to the data based on exponential rise and decay constants. The inset shows the expanded transients around time delay zero. The observed time shifts are indicated.

One color (400 nm / 400 nm) pump-probe experiments have also been performed (see Figure 4). Due to the fact, that pump and probe wavelength as well as intensities of both lasers are the same, the transients are symmetric with respect to time delay zero. The observed time constants are very similar to the one of the two color experiments and the width of the transients $Fe(CO)_{5\text{-}2}$ rises with the number of ligands lost, which corresponds to the increasing time shift of the 400/800 nm transients.

From all these results we conclude that the photodissociation of $Fe(CO)_5$ in the gas phase occurs on an ultrafast time scale (few hundreds of femtoseconds). This ultrafast time scale for the photodissociation process should exclude the possibility of statistical energy transfer within the molecule prior to fragmentation (IVR) or internal conversion, as it has been pointed out for the related $Mn_2(CO)_{10}$ molecule [8].

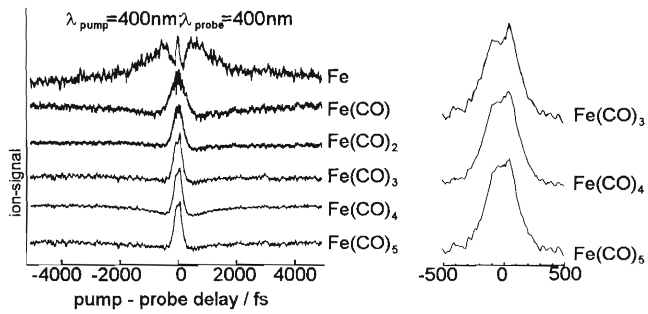

Figure 4 One color (400 nm / 400 nm) femtosecond transient ionization spectra of $Fe(CO)_5$ and of the fragments.

On the basis of the observed transients the following dissociation model can be proposed. $Fe(CO)_5$ is excited to a state with a total energy of 50,000 cm^{-1}. This state will evolve in a structural rearrangement. During the first 20±5 fs (the time shift observed in the $Fe(CO)_4$ transient) the $[Fe(CO)_5]^‡$ complex reaches a geometry which after ionization preferes to decay to a $Fe(CO)_5^+$ ion. The evolution of the multidimensional $[Fe(CO)_5]^‡$ complex continues until another configuration is reached after 30±5 fs. This new geometry of the complex now favors the production of $Fe(CO)_5^+$ ions, which undergo fragmentation into the measured $Fe(CO)_3^+$ ions. This is the origin of the $Fe(CO)_3$ transient. With a very similar interpretation, we can account for the observed $Fe(CO)_2$ transient. Within the model, the decay times of about 100 fs correspond to the dissociation time of $Fe(CO)_5$ into Fe(CO) + 4 CO. The measured transients for $Fe(CO)_{4\text{-}2}$ represent snapshots of the evolution of the multidimensional $[Fe(CO)_5]^‡$ transition state towards the loss of four CO-ligands yielding the Fe(CO) fragment. Furthermore, the ionization transient of Fe(CO) shows a rise time of 120±20 fs. This rise time matches the $Fe(CO)_5$ dissociation time of 100-150 fs discussed above. In addition, a decay to a time independent level is observed in the Fe(CO) with a time constant of 230±20 fs. This is an indication that at least two different, maybe excited, Fe(CO) fragments are formed in the dissociation, and only part of the Fe(CO) fragments decay further. This decay time is close to the observed rise time of 260±20 fs for the Fe fragment.

The ultrafast photodissociation of $Fe(CO)_5$ after fs excitation of the MLCT band with two 400 nm photons can be summarized as a two step process. The first step is a concerted loss of four CO ligands in about 100 fs. In the second step the formed Fe(CO) looses the last CO ligand within 230 fs.

1. $[Fe(CO)_5]^‡ \rightarrow Fe(CO) + 4\,CO$
2. $Fe(CO) \rightarrow Fe + CO$

Conclusions

The photodissociation of $Fe(CO)_5$ has been investigated in the gas phase using nanosecond and femtosecond laser pulses. Due to the ultrafast dissociation process, nanosecond laser pulses fail to ionize the parent molecule $Fe(CO)_5$. By the use of femtosecond laser pulses, ionization preceeds fragmentation and the ionized parent molecule is detected.
In addition, one and two color femtosecond pump-probe experiments have been performed by two photon excitation of the MLCT band with 400 nm femtosecond pump pulses and probe pulses of 400 nm and 800 nm. From the analysis of the transients in terms of rise and decay times, a model for the photodissociation of $Fe(CO)_5$ is proposed. In this model, $Fe(CO)_5$ dissociates up to Fe(CO) in a concerted fashion, *i.e.* the parent molecule looses after absorption of two 400 nm photons four CO-ligands on the time scale of a vibrational period of the Fe-CO bond. The measured $Fe(CO)_{4,3,2}$ ionization transients represent snapshots of the evolution of the multidimensional $[Fe(CO)_5]^{\ddagger}$ transition state on its way to Fe(CO). The excess energy is sufficient for a further dissociation of Fe(CO) into Fe and CO on a longer time scale.
More experiments using femtosecond lasers at different wavelengths and even shorter pulses are in preparation to provide additional information about the photodissociation dynamics of $Fe(CO)_5$ and of more complex metalorganic molecules in the gas phase.

Acknowledgments

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$Fe(CO)5$; ironpentacarbonyl, metalcarbonyl, multiphoton ionization, photodissociation, photodissociation dynamics, ultrafast, femtosecond, molecular beam, fragmentation, pump-probe, time-of-flight spectrometry