Femtosecond photodissociation dynamics of Fe(CO)5 in the gas phase

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Abstract

The photodissociation dynamics of Fe(CO)5 in the gas phase has been investigated by using femtosecond laser pulses at 400 and 800 nm. The parent molecule and all the fragment ions have been observed in a time-of-flight (TOF) spectrometer in real time. The photodissociation of Fe(CO)5 with the loss of four CO-ligands leads to Fe(CO) and takes place in about 100 fs. The ionization transients of the $Fe(CO)_{2-4}$ fragments are the fingerprints of the evolution of the transition state in the dissociation reaction. The subsequent fragmentation of Fe(CO) into Fe and CO occurs on a longer time scale of 230 fs. © 1997 Elsevier Science B.V.

1. 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] and, in addition, the complete photodissociation of these compounds has been applied in microelectronics as a means of growing thin ultrapure metal films onto surfaces [3]. Therefore, it has become important in recent years to understand the mechanism by which these complex molecules photodissociate loosing one or several CO groups. In the case of polynuclear metal carbonyls, the topic is to distinguish between the metal–metal and metal–ligand cleavage dynamics.

Fe(CO)5 has been considered, among others, as a prototype molecule whose study could provide a good

understanding of the mechanism of photodissociation. For this molecule, much theoretical information is available about its molecular and electronic structure [4–8] and many ab initio calculations have been performed in order to provide accurate values of the first and subsequent dissociation energies of the Fe–CO bonds, not only for the neutral Fe(CO)5 [8–10], but also for the ion molecule $Fe(CO)_5^-$ [11]. The theoretical results have been compared with experimental data obtained by different groups [12–15].

The energetics of this molecule is presented in Fig. 1 together with the measured gas phase absorption spectrum [6]. 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→ π^* transitions [6]. The absorption starts at about $25\,000$ cm^{-1} and shows two weak shoulders at $30\,300$ cm^{-1} and $35\,700$ cm^{-1} which have been assigned to ligand field (LF) d→d transitions
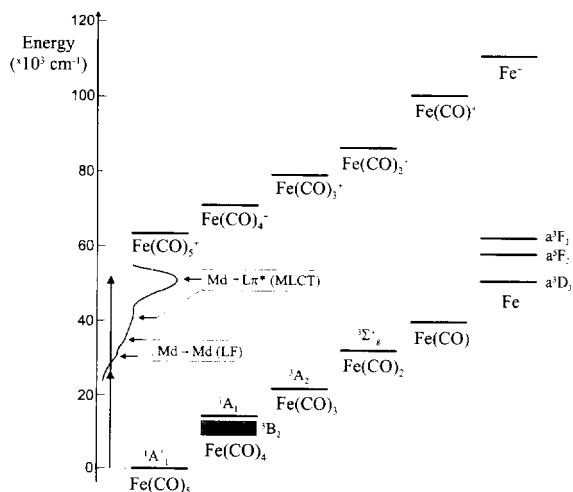
Fig. 1. The energetics of Fe(CO)$_5$ and a compilation of experimental and theoretical data of the neutral and ionic molecules. The gas phase absorption spectrum [6] is shown schematically and the assignments to LF and MLCT transitions are indicated by horizontal arrows. The shaded area corresponds to the range of calculated [9,10] energies for the electronic ground state of Fe(CO)$_4$. The vertical arrows indicate the two-photon excitation at 400 nm discussed in the text.

[6]. All the assignments are supported by theoretical calculations of several groups [5,6]. The most recent experimental value for the first ionization potential of Fe(CO)$_5$ was reported by Norwood et al. [14] (7.897 ± 0.025 eV; $63\,689$ cm^{-1}). The vacuum-ultraviolet (VUV) spectrum of Fe(CO)$_5$ was also measured [7]. Based upon ab initio calculations, two series of Rydberg states were assigned in the spectral ranges between $49\,600$ cm^{-1} and $61\,800$ cm^{-1} and between $64\,100$ cm^{-1} and $71\,800$ cm^{-1}.

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. After the pioneering works by Zare et al. [16] and Engelking [17], in which emission from electronically excited Fe atoms after laser excitation of Fe(CO)$_5$ was observed, Yardley et al. [18] were the first to measure the distribution of Fe(CO)$_n$ ($n = 2, 3$ and 4) fragments at different one-photon excitation excimer-laser wavelengths using a chemical trapping technique. They proposed a photodissociation process in which the CO ligands are lost sequentially. Their experimental results were in agreement with RRKM calculations in which only

one vibrational mode was coupled to the reaction coordinate (i.e. the motion of the CO-ligand with respect to the metal atom) and where about 65% of the available energy was retained by nascent Fe(CO)$_4$ as vibrational and/or electronic excitation. Grant et al. [19], using multiphoton ionization (MPI) to monitor the CO product after photolysis of the parent molecule in the region 290–310 nm, reported an inverted vibrational energy distribution in CO and an estimate of less than 0.6 ps for the lifetime of Fe(CO)$_5$ excited states in the 275–280 nm excitation region.

Later studies by Weitz et al. [20], Waller and Hepburn [21], and by Vernon et al. [22], using different techniques, were in agreement with a statistical sequential mechanism for the (excimer laser) photodissociation of Fe(CO)$_5$. In all cases (and even in the work of Yardley et al. [18]), the ultimate photodissociation product was Fe(CO)$_2$. It was argued [21] that the energy retained by the Fe(CO)$_2$ fragment, after absorption of one 193 nm photon and a sequence of three dissociations from Fe(CO)$_5$, was not enough to further dissociate Fe(CO)$_2$ into Fe(CO) and Fe. Vernon and coworkers [22] argued that a second photon has to be absorbed by the Fe(CO)$_2$ fragment in order to loose the two remaining CO ligands sequentially [22]. Photolysis laser wavelengths different than the ones provided by excimer lasers have also been used to study the electronic excited states of Fe (produced by multiphoton dissociation of Fe(CO)$_5$) via photoelectron spectroscopy (PES) [23,24] and laser induced fluorescence (LIF) [25]. Note that all nanosecond laser experiments failed to observe Fe(CO)$_5^+$ irrespective of the laser intensities and wavelengths used.

Several theoretical calculations suggested mechanisms for the photodissociation and an estimate of the involved time scales. Daniel et al. [5] were the first to propose for Fe(CO)$_5$ a non-adiabatic spin–orbit induced coupling between an excited singlet state and a triplet state correlating with the ground triplet state of the Fe(CO)$_4$ fragment. On the basis of this mechanism, Weitz et al. [20] and Waller and Hepburn [21] explained their experimental results. Recent theoretical studies by Daniel, Manz and coworkers on metal carbonyl hydrides [26,27] have proposed that the time scale for the cleavage of the metal–CO bond is as short as 100 fs.

Time-resolved experiments using ultrafast laser pulses were performed with metal carbonyls and

organometallics in solution (see Refs. [28-30]). The first gas phase experiment was recently reported by Zewail and coworkers [31] who studied the ultra-fast fragmentation dynamics of $Mn_2(CO)_{10}$. In this cornerstone experiment, the metal-metal and metal-ligand bond cleavage dynamics, occurring on a time scale of hundreds of femtoseconds, could clearly be distinguished. In a very recent experiment by Harris and coworkers [32], the dissociation dynamics of $M(CO)_6$ (M = Cr, W, Mo) in solution has been studied by femtosecond infrared (IR) spectroscopy. It was concluded that the formation of the metal pentacarbonyl fragment after ultraviolet (UV) photolysis of the parent molecule occurs in less than 240 fs, the resolution of their apparatus.

In this Letter, we report on the first 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 excitation and mass selected in a linear time-of-flight (TOF) spectrometer. Transient ionization spectra of the parent molecule and of every fragment have been measured by using the femtosecond pump-probe technique. From the results obtained in this study, 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 decay time. A mechanism is proposed to explain these observations. The results are also discussed in view of the photodissociation mechanisms found in the literature.

2. Experimental

The experimental setup has been described in detail elsewhere [33] and only a brief description will be given here. A home-built Ti:Sapphire oscillator yields pulsed femtosecond laser radiation centered at 800 nm with a duration of 50 fs. The femtosecond pulses are amplified in a modified commercial regenerative amplifier pumped by a 1 kHz Nd:YLF laser. The output of this system, after appropriate recompression, consists of pulses of 80 fs and of about 1 mJ energy per pulse at a wavelength of 800 nm. After second harmonic generation, the 400 nm and 800 nm lasers are 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 (see Fig. 2).

The molecular beam apparatus consists of two differentially pumped chambers one of them containing the $Fe(CO)_5$ source and the other one a linear time-of-flight (TOF) spectrometer. The $Fe(CO)_5$ sample, used without further purification (98%; Stream Chemicals), is taken directly from the cylinder at room temperature (vapor pressure of $\approx$ 40 Torr) and expanded through a nozzle of 50 μm.

The ions produced in the interaction region of the TOF spectrometer chamber are extracted and accelerated into the drift tube towards a microchannel plate (MCP) detector. The signal from the detector is recorded by a 500 MHz digital oscilloscope. 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 averaged to obtain sufficiently good signal-to-noise ratios. In all the experiments, the polarization of the pump laser was parallel to the TOF spectrometer axis, whereas the probe laser polarization was perpendicular to it. Changing the polarization of the pump and probe lasers did not affect the measured transients.

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 laser pulses.

3. Results and discussion

The TOF spectra obtained with the 400 nm and 800 nm lasers at intensities of about 10^{13} W cm^{-2} are represented in Fig. 3. As can be seen from the spectra, the parent molecule and all the fragments are observed at both wavelengths for these laser intensities. For the lowest laser intensities applied (about 10^{12} W cm^{-2}), the only mass peak observed was that of the parent
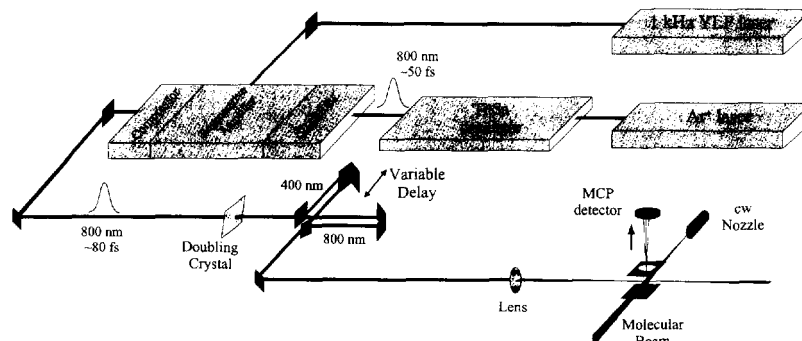
Fig. 2. Experimental setup showing the femtosecond laser system used in the present experiments. The ions produced by femtosecond laser excitation in a molecular beam are detected in a linear time-of-flight (TOF) spectrometer.
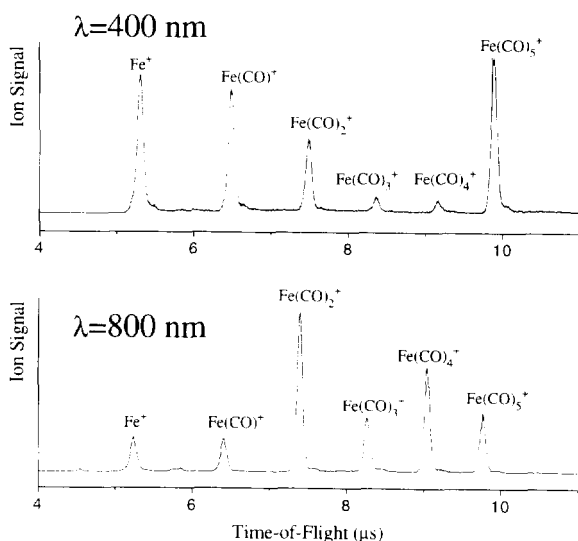

Fig. 3. Time-of-flight spectra obtained after irradiation of Fe(CO)₅ with femtosecond laser pulses at 400 nm and 800 nm.

ion. It is interesting to note that at least six photons of 800 nm are needed to ionize Fe(CO)₅. The fragment ion distribution was found to depend on both the wavelength and the intensity of the laser. These results indicate that for the applied intensities of about 10¹³ W cm⁻², the multiphoton fragmentation of the parent molecule is occurring most likely via dissociative ionization, i.e. ionization precedes fragmentation. A detailed analysis of the intensity and wavelength dependence of the ion spectra will be given in a forthcoming publication.

Fig. 4 shows the measured transient ionization spectra 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 less than 1% of the ion signal shown in Fig. 3. Therefore, the observed dynamics has to occur in the neutral molecule where the probe laser induces the ionization. In the 400 nm pump laser experiments, the absorption of two photons leads to an excitation of the strong band centered at around 50000 cm⁻¹ [6] (see Fig. 1). The very weak absorption observed at 25 000 cm⁻¹ [6] and the fact that more 800 nm probe photons would be needed to reach the ionization continuum support the two-photon excitation at 400 nm.

As can be seen from Fig. 4, the transients of the parent molecule and of the Fe(CO)₄ and Fe(CO)₃ fragments, show some ion signal before time zero, i.e. when pump (400 nm) and probe (800 nm) lasers interchange their role. In the case of the parent molecule, the ion signal at negative delay times < −300 fs is even larger than the signal at positive delay times. This effect strongly depends on the intensity of the pump and probe lasers. Several experiments were performed with the parent molecule and different attenuations of both lasers. As the intensity of the lasers was decreased, the ion signal for negative delay times was reduced practically to the same level as the ion signal for positive delay times. But the double peak structure of the transient in the very vicinity of time zero was retained. For the 800 nm pump laser, there are at least two possible excitations of the neutral molecule: a three-photon excitation to a LF state or a four-photon excitation to a MLCT state. The latter
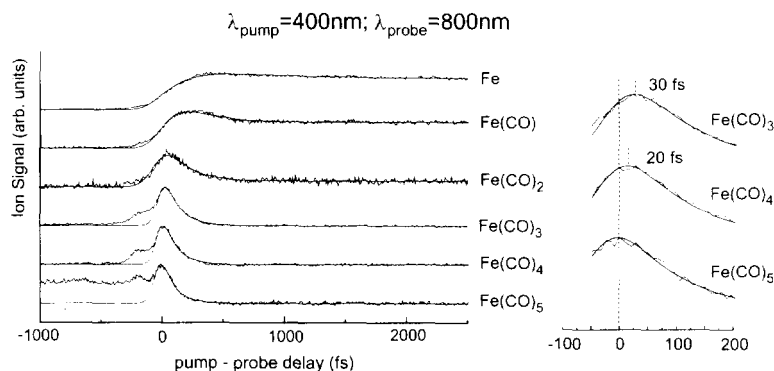
λ_pump=400nm; λ_probe=800nm

Fig. 4. Femtosecond transient ionization spectra of the parent molecule and of the fragments. The measurements were made with attenuated pump and probe lasers yielding less than 1% of the ion signal of Fig. 3. The solid lines represent the fits to the data based on exponential rise and decay constants. The inset shows the expanded transients around time zero for the parent molecule and the $Fe(CO)_4$ and $Fe(CO)_3$ fragments. The observed time shifts of the transients are indicated.

excitation is similar to the one obtained after absorption of two photon of 400 nm. It is possible that part of the signal observed for negative and positive delay times correspond to the same process. In addition, a process is initiated which shows no time dependence on the measured time scale. In the following, that part of the transients is analyzed for which the pump excitation is at 400 nm 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 Fig. 4 as solid lines. The rise and decay time constants obtained are listed in Table 1. The parent mass transient and the transients of the fragments $Fe(CO)_4$ and $Fe(CO)_3$ were fitted to single exponentials with decay times of 100 ± 5 fs, 105 ± 5 fs and 115 ± 5 fs, respectively. In addition, $Fe(CO)_4$ and $Fe(CO)_3$ transients show time shifts of 20 ± 5 fs and 30 ± 5 fs, respectively, with respect to the maximum of the $Fe(CO)_5$ signal. The $Fe(CO)_2$ transient consists of no appreciable rise time (< 20 fs), a decay time of 150 ± 20 fs to an asymptotic level, which is constant for more than 100 ps, and again a time shift of 50 ± 5 fs. The $Fe(CO)$ transient was fitted with a rise time of 120 ± 20 fs and a longer decay time of 230 ± 20 fs. For the $Fe(CO)$ transient the asymptotic level was considerably higher than for the $Fe(CO)_2$ (the ratio of

Table 1
Rise and decay time constant for the parent molecule and the fragments

	τ_{decay} (fs)	τ_{rise} (fs)
$Fe(CO)_5$	100 ± 5	–
$Fe(CO)_4$	105 ± 5	–
$Fe(CO)_3$	115 ± 5	–
$Fe(CO)_2$	150 ± 20	< 20
$Fe(CO)$	230 ± 20	120 ± 20
Fe	490 ± 50	260 ± 20

the decay amplitude to the amplitude of the time independent contribution was ≈ 10 for the $Fe(CO)_2$ transient vs. ≈ 2 for the $Fe(CO)$). 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 with a ratio of amplitudes (decay to time independent contribution) of ≈ 1.

The ultrafast decay time measured for $Fe(CO)_5$ excludes the existence of intramolecular vibrational energy redistribution (IVR) before dissociation, as this process should happen on a considerably longer time scale, as it has been pointed out by Zewail and coworkers for $Mn_2(CO)_{10}$ [31]. Other non-radiative processes, such as internal conversion to the electronic ground state, followed by dissociation from a highly vibrationally excited state, are also very unlikely [31].

In the present experiments, the parent molecule is excited to a total energy of 50 000 cm^{-1}. A MLCT-

type singlet state could be a good candidate for such an excitation, as it has been pointed out elsewhere [20,21]. A non-adiabatic crossing to a triplet state may take a few ps for this molecule, since the spin–orbit coupling is very small for the first row transition metal complexes [27,34]. Therefore, it is most likely that the dissociation of $Fe(CO)_5$ proceeds directly from the optically pumped singlet state up to some electronically excited singlet state of the fragments.

The available energy for $Fe(CO)_5$ after absorption of two photons of 400 nm is enough to break the five Fe–CO bonds (see Fig. 1). A further issue is whether the ultrafast dissociation of $Fe(CO)_5$ occurs stepwise or in a concerted fashion. Concerted here means that the CO-ligands leave the parent molecule on the time scale of a vibrational period. The main difference between a stepwise and a concerted process is whether or not stable intermediate species are observed. On a first glance, the present results seem to indicate that the mechanism is a stepwise fragmentation, since all the fragments are observed. However, $Fe(CO)_5$ and the largest fragments, $Fe(CO)_4$ and $Fe(CO)_3$, show very similar decay times (100–115 fs) and no detectable rise time. Even $Fe(CO)_2$ does not show any appreciable rise time but a fast decay of 150 fs. In addition, the transients of the fragments exhibit a time delay of several tens of femtoseconds with respect to the parent molecule. The fact that we are observing practically the same time decay for the parent and the $Fe(CO)_{n=2-4}$ fragments suggests that the same intermediate state dynamics determines these transients.

A model consistent with these observations is as follows: $Fe(CO)_5$ is excited to a state with a total energy of $50\,000$ cm^{-1} (most probably a MLCT singlet state). This state will evolve in a structural rearrangement during the first 20 fs. At this particular geometry of the $[Fe(CO)_5]^{\ddagger}$ complex, the system absorbs probe laser photons yielding parent ions which undergo fragmentation into the measured $Fe(CO)_4^+$. The time scale of this ionic fragmentation is yet unknown. The evolution of the multidimensional $[Fe(CO)_5]^{\ddagger}$ complex continues until another configuration is reached after 30 fs. This new geometry of the complex now favors the production of $Fe(CO)_5^+$ ions which undergo fragmentation into $Fe(CO)_3^+$. 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 $Fe(CO)+4CO$. The measured transients for $Fe(CO)_{2-4}$ represent snapshots of the evolution of the multidimensional $[Fe(CO)_5]^{\ddagger}$ transition state towards the loss of four CO-ligands yielding the $Fe(CO)$ fragments. Fig. 5 shows a pictorial representation of the model.

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 100–115 fs discussed above. In addition, a decay to a time independent signal level is observed 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. This decay time is close to the observed rise time of 260 ± 20 fs for the Fe fragment. However, if the Fe fragment was formed sequentially, the rise should be biexponential with one time constant corresponding to the decay of the $Fe(CO)_5$ parent molecule into $Fe(CO)$ (about 100 fs) and a second one corresponding to the decay of $Fe(CO)$. But the analysis shows that the Fe transient could be fitted perfectly with a single-exponential rise. The apparent absence of the 100 fs time constant in the rise of the Fe transient can be understood just by taking into account that only a small part of the $Fe(CO)$ fragments undergo further fragmentation into Fe and CO. Finally, we observe a long decay time of about 490 fs for the Fe fragment. Since Fe atoms cannot decay in such a short time, even if they are produced in highly excited states, this decay must be related to a process whose origin is in the precursor $Fe(CO)_5$ parent molecule or the $Fe(CO)$ fragment.

The idea of a concerted loss of ligands has been discussed by Jackson [35] for the related $Cr(CO)_6$. In that work, the fluorescence of electronically excited Cr atoms obtained after the photodissociation of $Cr(CO)_6$ produced by nanosecond laser excitation was measured in a gas cell at different pressures. The main conclusion of those experiments is that when the excitation energy is high enough (corresponding to multiphoton absorption of the parent molecule) the dominant photodissociation mechanism is a concerted one. The parent molecule absorbs two, three or more photons coherently and a highly excited electronic state of the complex is prepared. This state will dissociate explosively, loosing several ligands simultane-
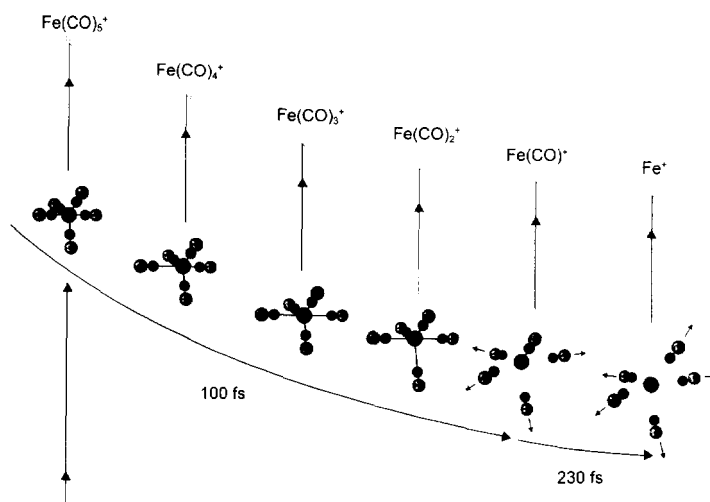
Fig. 5. Pictorial representation of the model proposed for the photodissociation mechanism of Fe(CO)₅. Electronically excited Fe(CO)₅ dissociates into Fe(CO)+4CO in about 100 fs. The ionization transient spectra measured for the Fe(CO)₂₋₄ fragments represent snapshots of the evolution of the multidimensional [Fe(CO)₅]‡ transition state on its way to dissociation. The last Fe-CO bond cleavage occurs on a longer time scale of 230 fs.

ously, in a time scale of just a single vibration. The dissociation process can be visualized then as a half-collision reaction, where the highly excited state of the parent molecule can cross onto multiple potential energy surfaces, each of them representing a different product metal containing fragment. To which extension this process occurs will depend on the available energy. Jackson [35] concluded that a sequential mechanism could gain more importance with respect to the concerted loss of ligands as the excitation energy decreases. Our results are in qualitative agreement with these conclusions. The Fe(CO)₅, electronically excited to 50 000 cm⁻¹, looses four CO-ligands in just 100 fs. As typical vibrational periods of the Fe-CO bonds are between 80-100 fs [8], this can be termed a concerted loss of the first four ligands. The subsequent dissociation of the formed Fe(CO) occurs on a longer time scale. After the explosive loss of up to four CO-ligands following excitation of the parent molecule, the available energy is still large enough to initiate the rupture of the last Fe-CO bond, yielding Fe atoms.

4. Conclusions

The femtosecond dynamics of the photodissociation of Fe(CO)₅ has been investigated in a molecu-

lar beam. The parent ion and every fragment ion have been observed in time-of-flight (TOF) spectra for different laser wavelengths. Transient ionization spectra of the parent molecule and of the different fragments were measured using the femtosecond pump-probe technique. The time resolution in the experiments was sufficient to resolve the primary dynamics of the photodissociation of Fe(CO)₅ and the subsequent loss of all CO-ligands.

On the basis of our analysis, we conclude that Fe(CO)₅ dissociates up to Fe(CO) on a very short time scale of about 100 fs. We propose a model by which the measured ionization transients of the Fe(CO)₂₋₄ fragments represent snapshots of the evolution of the multidimensional [Fe(CO)₅]⁺ transition state on the way to the multiple-ligand loss. The Fe(CO) fragment further dissociates and looses the remaining CO-ligand on a longer time scale of 230 fs. Nanosecond laser experiments failed to observe Fe(CO)₅⁺ and the CO containing fragment ions because of the ultrafast fragmentation dynamics revealed in the present femtosecond experiments.

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 in the gas phase.

Acknowledgements

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