Transient Midinfrared Study of Light Induced Dissociation Reaction of Ru(dcbpy)(CO)$_2$I$_2$ in Solution

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Illumination of Ru(dcbpy)I$_2$(CO)$_2$ (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) with (near) ultraviolet light induces dissociation of one of the CO groups of the complex. In solution the opened coordination site of the metal is occupied by a solvent molecule. In the present study the kinetics of the ligand exchange reaction has been studied in solution with femtosecond time resolution by probing the CO stretching vibrations of the reactant and the product molecules Ru(dcbpy)I$_2$(CO)(EtOH) in the infrared and probing electronic transitions in the visible spectral regions. The kinetic results indicate that photoelimination of the CO group occurs on a subpicosecond time scale. The overall quantum yield of the reaction is well below unity (0.3), indicating that the majority of the excited parent molecules does not convert to the product molecules. According to the present observations, recovery of the parent molecule takes place on a subpicosecond time scale. Later time evolution shows relaxation of this state with time constants of 4 and 68 ps. Dissipation of the excess energy of the solvated product is characterized by a biexponential relaxation process with time constants of 18 and 270 ps.

1. Introduction

The motivation to study transition metal carbonyls is in their use as photocatalyst in several industrial and synthetic reactions. A primary step in these reactions is photodissociation of one or more CO groups that produce coordinatively unsaturated species.[1−3] The efficiency of the CO dissociation and the chemical nature of the intermediate species are important factors that determine the catalytic activity of these complexes.

Photodissociation reaction of transition metal carbonyls and their subsequent reactions have been intensively studied by transient absorption spectroscopy in the visible region[4−7] and in the IR.[8−12] In the gas phase, elimination of the first CO group is followed by thermal dissociation of further CO ligands,[13−16] whereas in solution the excess thermal energy is dissipated by vibrational cooling and the vacant site in the coordination sphere of the metal center is reoccupied by a solvent molecule.[8,9,17] According to earlier studies of transition metal carbonyls, dissociation of the carbonyl group is an extremely fast process (<100 fs).[6,18−21] It has been observed both experimentally and theoretically that dissociation is not a direct process but involves electronic relaxation from initially excited state.[16,22] In the case of transition metal hexacarbonyls (M(CO)$_6$) the relaxation is ultrafast, leading to avoided crossing to a repulsive surface and photochemical dissociation of one CO group in less than 100 fs. On the other hand, for example, formation of a solvent complex or solvation of Cr(CO)$_5$ is a much slower process taking place in 1−2 ps.[4,6] It has been suggested that solvent coordination occurs before equilibrium has been established, and the structure of the solvated complex is initially determined by the statistical nature of the solvation process.[5,23] Then the complexes rearrange to form the most stable nuclear configuration on a slower time scale. However, Harris and co-workers observed that in ethanol Cr(CO)$_5$ is preferably solvated via the hydroxyl end of the solvent and therefore the solvation process does not follow statistical behavior.[23] The newly born molecule has excess energy, and solvent complexation is therefore followed by vibrational cooling. In some cases solvation may require reorganization of the five-coordinated metal fragment. In weakly coordinating solvents the solvent coordination energy may not be sufficient to compensate the reorganization energy loss, and thus the unsolvated complex may be thermodynamically more stable.[8] For instance, it has been observed that in Ar or N$_2$ matrixes[24] or in hexane solution[8] unsolvated Re$_2$(CO)$_9$ is the most stable species. The overall quantum yield of the ligand exchange reaction is typically well below unity, indicating that part of the photodissociated five-coordinated species recombine with CO groups.[17,25]

We have carried out UV pump−IR probe experiments with 320 nm excitation to study photodissociation of the (*trans*-I)-Ru(dcbpy)I$_2$(CO)$_2$ complex in ethanol. Infrared transient absorption spectroscopy is a powerful method that provides structurally specific information on the studied system. In the present case we can clearly distinguish the reactant and the product molecule absorptions in the IR region, which is not straightforward with complexes containing several carbonyl ligands.[17,26] The relatively simple IR spectrum shows only two carbonyl stretching modes of the parent molecule and one CO stretching mode of the product, all spectrally well separated. Moreover, previous structural studies give the main features of the mechanism of the ligand exchange reaction.[27] The UV excitation breaks an equatorial Ru−CO bond after which the remaining ligands reorganize around the metal atom, and a solvent molecule is attached to the opened axial site. To shed light on the dynamics of the reaction, we have probed re-formation of the parent

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molecules in the ground state and formation of the product. This study concentrates on relaxation processes of the parent and solvated product molecules. We also discuss the observed IR kinetics together with results from the transient visible spectroscopy of the same reaction.

2. Experimental Section

The details of the synthesis of the studied molecule are given elsewhere.[27] For the transient absorption measurements the samples were dissolved in ethanol. Steady state UV-vis absorption spectra were measured with a Varian Cary100 absorption spectrophotometer and steady state IR spectra were recorded with a Nicolet Magna 760 FTIR spectrometer. To measure the steady state spectrum of the product, the solution was illuminated with a tungsten lamp (150 W). In the transient IR measurements the sample was pumped trough a jet with a nominal thickness of 100 μm, whereas in the transient visible measurements a flow cell with thickness of 1 mm was used.

The experimental setup for the UV pump−IR probe experiments, based on a home-built amplified Ti:sapphire laser, has been described in detail previously.[28] The near-UV pulses for electronic excitation were generated by sum frequency mixing of the Ti:sapphire fundamental and visible pulses obtained by a noncollinear optical parametric amplifier.[29] The excitation wavelength was tuned to 320 nm, the pulse energy was 2.4 μJ, and the pulse duration around 50 fs. The mid-infrared probe pulses were generated using double-pass collinear optical parametric amplification in a BBO crystal, followed by difference frequency mixing of signal and idler in a GaSe crystal.[30] The center frequency was tuned to 2025 cm^{-1} and the output energy was about 1 μJ. Pump and probe pulses were then combined in a standard excite and probe scheme, where the UV pulses could be variably delayed and were focused with a concave mirror on the sample with a spot diameter of approximately 180 μm. Probe and reference pulses were obtained using reflections from a BaF$_2$ wedge (10 nJ/pulse) and focused in the sample with off-axis parabolic mirrors (spot size about 100 μm). Probe and reference pulses were dispersed in a grating spectrometer after passing the sample, and complete spectra were recorded simultaneously for each shot using a liquid nitrogen cooled 2×31 HgCdTe detector array. Normalization of probe and reference signal on a single shot basis as well as synchronous chopping of the UV pump pulses provided highly reliable transient absorption spectra, allowing the detection of absorption changes, ΔOD, as small as 0.05 mOD. The optical density of the sample at excitation wavelength 320 nm was ~1. For reference purposes, the time resolution (fwhm 130 fs) and the zero time delay point were determined by a cross-correlation experiment performed in a polished ZnSe window. All IR data were measured in both perpendicular and parallel polarizations between the UV pump and IR probe. For data analysis, the signal was calculated as $I_{par} + 2I_{perp}$ to deduce the molecular dynamics not affected by rotational diffusion.

The visible transient absorption measurements were carried out by using the following equipment. Femtosecond pulses were generated in a mode locked Ti:sapphire oscillator (Coherent Mira 900) pumped with a diode-pumped frequency-doubled Nd:YVO$_4$ laser (Coherent Verdi-5W). Pulses were amplified with a multipass Ti:sapphire amplifier (Quantronix Odin). The laser system produces 100 fs pulses at 790 nm with 1 kHz repetition rate and 900 μJ pulse energy. Cross-correlation of pulses in a BBO crystal was used to estimate the pulse duration. The excitation pulses at 395 nm were generated by frequency doubling the fundamental laser frequency in a BBO crystal. The probe and the reference pulses were taken from white light continuum (450−1000 nm) generated by focusing a fraction of the fundamental laser beam into a 2 mm thick sapphire plate. A monochromator (Acton SpectraPro 150i) with a spectral bandwidth of 9 nm was used to select the probe wavelength after the sample. Intensities of each excitation, reference, and probe pulse were recorded and digitized with a detection system based on photodiodes. The signal was recorded as the change of optical density (OD) in the sample. The optical density at the pump wavelength (400 nm) was 0.2.

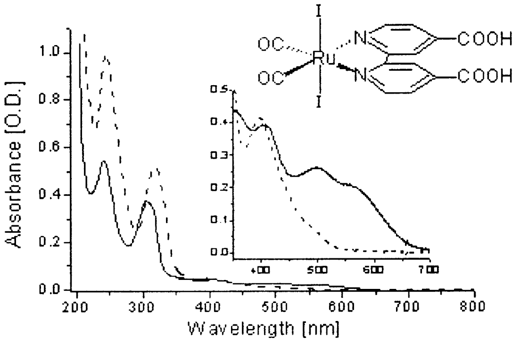

Figure 1. Steady state absorption spectra of the reactant (dashed line) (concentration 1 × 10^{-5} M) and the product (solid line). The inset shows absorption spectra of 5 times more concentrated solutions in the visible region. The structure of the reactant molecule is also shown.

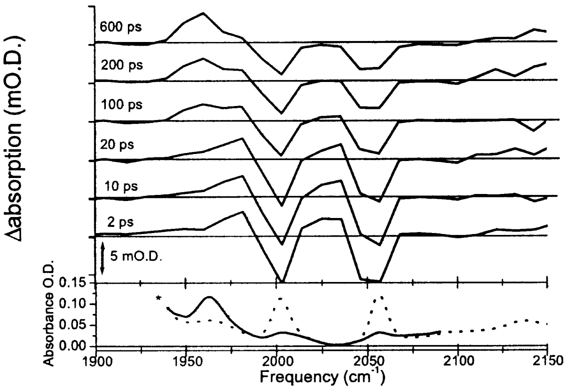

Figure 2. Transient IR spectra of the reaction solution as a function of time. The lowest panel shows steady state IR spectrum of the parent (dashed line) and the product (solid line) in ethanol, respectively. The steady state spectra are not shown below the asterisk (1940 cm^{-1}) due to strong absorption of the solvent.

3. Results

Figure 1 shows the steady state UV−vis absorption profiles of the reactant and the product molecules. The reactant is weakly absorbing in the visible region but shows two distinct absorption bands in the UV region at 320 nm and at 230 nm, respectively. Illumination with UV light increases absorption in the visible and a new band appears at 560 nm. This is a clear indication of formation of a photoproduct. Steady state IR absorption spectrum of the parent molecule Ru(dcbpy)I$_2$(CO)$_2$ in ethanol shows two absorption bands around 2000 cm^{-1}: a symmetric CO stretching vibration at 2056 cm^{-1} and an antisymmetric one at 2001 cm^{-1} (Figure 2, the lowest panel). UV illumination of the sample induces spectral changes that can be unambiguously ascribed to a photodissociation reaction. The photodissociation product has only one absorption in the CO stretching region at 1962 cm^{-1}, well separated from the reactant bands. Transient IR spectroscopy was used to study time evolutions of these absorptions after excitation. Figure 2 shows the transient infrared

TABLE 1: Relative Magnitudes of the Multiexponential Temporal Components[a]

wavelength	4.3 ± 0.3 ps (%)	70 ± 5 ps (%)	270 ± 10 ps (%)	constant (mOD)
1960 cm^{-1}			−100	4.1
2001 cm^{-1}		−100		−3.9
2024 cm^{-1}	33	67		−0.05
2035 cm^{-1}	−47	100		−0.2
2057 cm^{-1}	−21	−79		−3.2
520 nm	23	46	30	1.1
560 nm	32	25	42	1.4
790 nm	23	77		0

[a] Negative values correspond to rising and positive values to decaying components. The scaling constant is shown in the right column.

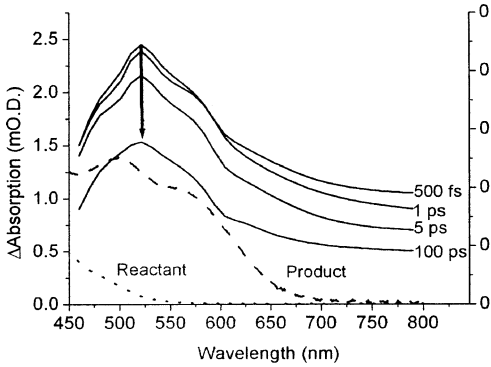

Figure 3. Transient absorption spectra of the reaction in the visible region at time delays 500 fs, 1 ps, 5 ps, and 100 ps. The dotted line represents the steady state absorption of the parent and dashed line steady state absorption of the solvated product. The arrow indicates the changes in transient absorption spectra as a function of time.

spectrum of the studied complex in ethanol solution at different delays between the UV pump and the IR probe. Immediately after excitation the two parent molecule bleach signals appear within the instrumental response time, and the 1962 cm^{-1} band is formed. This absorption is assigned to the CO stretching mode of the photolysis product Ru(dcbpy)I$_2$(CO)(EtOH). In addition, increased absorption is seen on the low-frequency side of the parent molecule absorptions at 1981 and 2024 cm^{-1}. The photobleached parent molecule absorptions at 2056 cm^{-1} and at 2001 cm^{-1} recover with the same time constants of 4.3 and 70 ps as the induced absorptions at 1981 and 2024 cm^{-1} decay. This indicates that they are most probably related to the same process. The other induced absorption around 1962 cm^{-1} is formed within the time resolution of the experiment and later delays show a rise time of 270 ps. The parent bleach signal level stays at ~3.5 mOD, 60% of the initial bleach, after 200 ps (see Table 1). At long delays (>600 ps) the product molecule absorption ~1960 cm^{-1} remains constant (4 mOD). Transient IR measurements were carried out using both parallel and perpendicular polarizations between the UV pump and the IR probe. From the anisotropy data it is possible to calculate of the angle between the UV and IR transition dipoles at zero delay.[31] The estimation gives the values 42 ± 2° and 81 ± 2° as the angle for the bleach signals at 2003 and 2057 cm^{-1}, respectively. Anisotropy decay of the parent molecule bleach gives 250 ps as a rotation correlation time of the molecule assuming that the molecule is a symmetric rotor.

We have also measured the transient absorption spectrum of the complex in solution in the visible region (Figure 3). The ground state parent molecule absorbs only weakly in the visible region but the excited states show stronger absorptions. Also the ground state of the solvated product molecule Ru(dcbpy)I$_2$(CO)(EtOH) has an absorption bands peaking at 500 and 560 nm. The kinetics of the reaction was probed over the region 460−790 nm to investigate the time dependent spectral changes and compare them to the previously gathered transient data of the parent molecule in frozen solution.[32] This information is helpful in resolving the mechanism of the geminate recombination. The problem with interpretation of the data collected in the visible region is that the induced absorptions arising from the parent molecule and the CO dissociation product overlap each other. The maximum intensity of the signal is attained at wavelengths where the product molecule has an absorption maximum (520 nm). At these wavelengths the transient absorption signal remains positive whereas in the low energy side of this absorption, where the ground state of the product does not absorb, the signal decays to zero. This observation is interpreted as an indication of formation of a stable photoproduct of the reaction. In principle, the same information about the system can be extracted from the measurements also in the IR region. In fact, it turned out that the decay of the transient absorption signal is very similar in the IR and in the visible, and it is possible to fit the data by using the same kinetic constants of 4.3, 70, and 270 ps (see Table 1 and Figure 4)

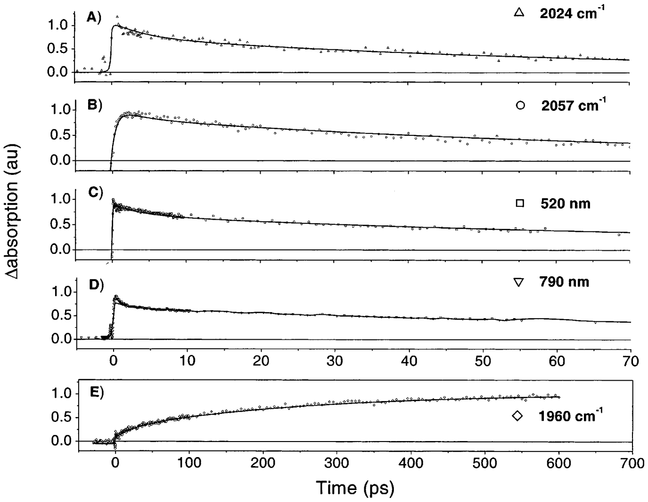

Figure 4. Decay of the hot parent molecule in the IR at (a) 2024 cm^{-1} and (b) 2057 cm^{-1}. The latter signal is multiplied by (−1). Decay of the signal in the visible region (c) at the wavelength where the product molecule has absorption (520 nm) and (d) where the product molecule does not absorb (790 nm). At 2057 cm^{-1} and at 520 nm, baseline is corrected in a way that at long delays (600 ps) signal decays to zero. The lowest panel (e) shows transient absorption kinetics of the product band at 1960 cm^{-1}. Notice the different scale of the *x*-axis.

4. Discussion

The quantum yield of the studied reaction has been determined to be 0.3 at 458 nm excitation, indicating that 70% of the excited parent molecule turn back to the reactant ground state.[27] Several models can be used to explain the nonunity quantum yield and experimental observations of the transient IR absorption measurements. In the simplest model the dissociation reaction involves direct population of the dissociative potential energy surface. Then, due to the cage effect provided by the solvent the CO is recombined with the five-coordinated intermediate and a hot parent molecule is re-formed in the electronic ground or the excited state. On the other hand, the mechanism may involve competing channels of relaxation of the excitation: dissociation and internal conversion or intersystem crossing to lower lying states.[16,34,35]

In the transient IR experiment the parent molecule absorptions do not fully recover (see Figure 2). This is an indication that a

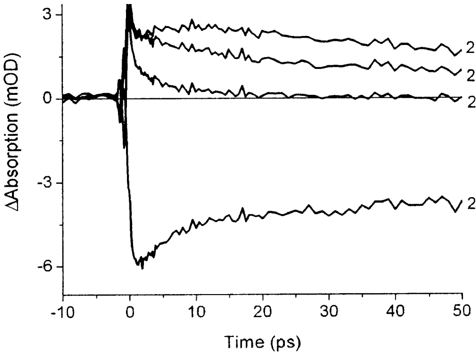

Figure 5. Kinetics of the hot parent molecule at frequencies below the fundamental absorption at 2057 cm^{-1}. The fastest rise time, after the spike signal, and the fastest decay time 4.3 ps is observed at 2021 cm^{-1}. The slowest rise time 4.3 ps is observed at 2043 cm^{-1}.

fraction of the parent molecules are transformed into product molecules. However, only ~45% recovery of the bleach signal was observed instead of 70%, as expected from the quantum yield measurements. This may indicate that part of the parent molecules recover faster than our time resolution. Immediately after excitation the transient spectrum shows induced absorptions on the red side of the parent molecule transitions at 2024 and 1981 cm^{-1}(Figure 2). These bands are assigned to excited state absorption of the hot parent molecule and are red shifted by ~20−30 cm^{-1} due to anharmonicity.[26,33] The instrument response time limited rise of the absorption at 2021 cm^{-1} is another indication of the subpicosecond recovery of the hot parent molecules (Figure 5). This sort of behavior may be observed because the majority of the excited molecules undergo ultrafast internal conversion to a hot ground state and only a smaller fraction dissociate. On the other hand, if all molecules dissociate but a fraction of them undergoes geminate recombination ending up on an electronic ground state on sub-200 fs time scale, a similar signal should be seen. Therefore, the time resolution of the experiment does not allow us to distinguish whether the recovery is due to internal conversion, geminate recombination or both.

Formation of the CO dissociation product of Ru(dcbpy)I$_2$(CO)$_2$ is seen in the transient infrared spectrum as an increase of a new absorption band at 1960 cm^{-1}. The new absorption is initially broad, extending to 1930 cm^{-1}. The rise time of the band is limited by the instrumental response, indicating that the formation of the dissociation product occurs on sub-200 fs time scale. In principle, the geminate recombination should be seen as a decay of this signal. Unfortunately, the initial absorption is very broad and unstructured and the high-frequency edge of the product molecule absorption overlaps with the hot parent molecule absorption around 1980 cm^{-1}. These features make the analysis of the early moments of the signal difficult. Because no decay of the signal was observed at later time delays, it indicates that no recombination occurs or the recombination is faster than the time resolution of the experiment. In the CO dissociation process the molecule is moving along a dissociative potential surface, that is, along the Ru−CO stretching coordinate. The dissociated CO is colliding with the repulsive wall provided by the first solvent shell, which greatly increases the probability for recombination. If the CO is able to escape from the solvent cage, recombination becomes very unlikely. On the other hand, after the solvation is complete, the open position in the coordination sphere of the metal center is occupied by a solvent molecule, and CO recombination is not possible anymore. Furthermore, from the experimentally determined crystal structure we know that iodine atoms in the molecule change their position from trans to cis prior to solvent coordination.[27] It is reasonable to assume that the change in coordination and the solvation are slower processes than recombination because both of these processes require movement of heavier atoms or groups. Then, the faster process, that is the recombination, is also the more probable process. After recombination the parent molecule releases significant amount of excess energy, which can be expected to localize, at least transiently, to the CO stretching. This, in fact, supports the assumption that most of the photodissociated CO groups are recombined with the five-coordinated intermediate, and that this process is sufficiently fast. In other transition metal complexes the cage recombination is shown to occur after a few collisions in the solvent cage over about 150 fs.[17]

The rise of the induced absorption is slower at the frequencies closer to parent ($v = 1$) ← ($v = 0$) transition (1957 cm^{-1}). The frequencies below the fundamental absorption correspond to transitions from higher vibrational levels. Due to excess excitation energy after recombination and/or internal conversion the parent molecules occupy a distribution of quantum states associated with the CO stretching motion. Relaxation of the hot parent molecule along the vibrational ladder ($v = 0$) ← ($v =$ high) is seen as a slower rise of the signal the closer the detection frequency is to the ($v = 1$) ← ($v = 0$) transition (Figure 5).[34] The hot parent molecule absorptions decay with the same time constants of 4.3 and 70 ps as bleaches of the parent molecule recover. Vibrationally hot molecules in liquids have been observed to cool in this time scale.[33] The corresponding pair of constants that describe cooling of the product molecule is 18 and 270 ps. Cooling of the product is seen as narrowing of the product absorption band around 1960 cm^{-1}. At the edge of this absorption band at 1935 cm^{-1} the product absorption band decays with a time constant of 18 ps, and at 1960 cm^{-1} the signal rises with a time constant of 270 ps. Biexponential relaxation kinetics may also result from cooling of the highly excited CO stretching mode and cooling of the other (low) frequency modes anharmonically coupled to it.[11,26,28,40] Therefore, it may be concluded that the observed changes of the transient absorption signal are related to intramolecular vibrational redistribution of the parent and product molecules and energy dissipation to the solvent.

Quantum chemical calculations and UV−vis spectra suggest that there are several states between the initially excited state and the ground state. It is also known that in corresponding ruthenium complexes intersystem crossing to triplet states occurs in less than 100 fs, indicating that probably also triplet states are involved in the relaxation processes.[36−38] Therefore, it is possible that internal conversion/intersystem crossing from the optically excited state to ground state takes place via an intermediate state/s or that after geminate recombination the parent molecule ends up in an excited intermediate state, which may also be a triplet state. Because the density of states is high it is very likely that relaxation between states is ultrafast. We do not observe transient features that would clearly indicate relaxation between different excited states before ending up in the ground state. That might be because several states are involved in the relaxation process and spectra of different transients overlap. The other option is that the relaxation is faster than time resolution of the experiments.

To get an idea of the relaxation processes between the electronic states, one can compare the data obtained by using different excitation wavelengths. In the IR measurements UV excitation at 320 nm was used, whereas for probing in the visible the excitation wavelength was 395 nm. Therefore, the initial excitation prepares the parent molecule in different states in these two cases. According to previous calculations the UV pulse centered at 320 nm excites mostly the dcbpy ligand centered $\pi^* \leftarrow \pi$ transition, whereas the 395 nm excitation promotes the electron to a mixed ruthenium−iodine orbital.[32] As shown in Figure 4, the kinetics measured in the IR and in the visible regions are very similar. This observation indicates that after the first picosecond the same relaxation process is probed independent of excitation and, therefore, either before or after dissociation the relaxation between electronic states is very fast.

To understand better the role of excited states in the reactant and the product complexes, we have measured the kinetics of the parent and product molecules separately.[32] Femtosecond transient absorption measurements reveal the dominance of excited state absorption over the whole visible region, as predicted also by calculations. It was observed that in frozen ethanol rigid surroundings prevent the ligand exchange reaction.[32] This can be associated with the strong cage effect provided by the frozen solvent, which mostly overcomes further reactions after dissociation. At low temperatures the parent molecule shows temperature dependent long lived emission (λ_{max} = 650 nm). This emission is only seen at low temperatures and is quickly quenched when the temperature is increased above 120 K as new channels are opened for relaxation of excitation.[27] Furthermore, excited state absorption decays in nanoseconds. Such behavior can be considered as clear evidence of excited states being involved in the relaxation process of the recombined parent molecule. To summarize, within the first few hundreds of femtoseconds geminate recombination or internal conversion/intersystem crossing cause a rapid channelling of excitation into highly excited states of the parent molecule. Transient absorption kinetics show strong indications that the relaxation pathways go through intermediate electronically excited states, rather than through conversion into the vibrationally hot electronic ground state.

The dissociated molecules that are able to escape from the solvent cage undergo conformational change followed by solvation. The bond dissociation energy of the Ru−C bond is 175 kJ/mol.[39] Thus excitation at 320 nm (372 kJ/mol) results in a considerable amount of excess energy for the five-coordinated product after CO dissociation. The observed narrowing of the absorption band at 1960 cm^{-1} is an indication of dissipation of energy by vibrational cooling, which may result from relaxation of the CO stretching vibration and low-frequency vibrational modes coupled to it.[26] The faster cooling component (18 ps) is comparable to the rates reported by other groups, for instance 15−25 ps for $Mn_2(CO)_9$ depending on the solvent.[40] The other component (270 ps) seems, however, somewhat slower than what has been reported for other transition metal carbonyls (∼145−170 ps).[26,40] The difference may be due to the smaller amount of excess energy available for the solvated product in the present complex.

To find out the time scale of solvent attachment, the measurements in the visible region were carried out in several alcohol solutions, in methanol, in ethanol, and in pentanol. Because the shape of the steady state absorption of the solvated product molecule is dependent on the solvent, we expected to see a difference in the transient absorption signals due to different solvent molecule attachments in the vacant coordination site. However, the decay of the transient absorption signals in all these solvents were almost identical, indicating that the solvent attachment is faster than a few picoseconds. This is, indeed, in accordance with the earlier studies reported in the literature.[4,6] In several studies it has been assumed that the product molecules are formed in the excited state.[6,17] The present measurements do not give a definite answer to whether the product is born in the ground state or in an excited state but the long rise component (270 ps) may indicate that electronically excited states are involved in the relaxation process.

5. Summary

Photochemical dissociation and the subsequent events in Ru(dcbpy)$I_2(CO)_2$ were studied by transient absorption spectroscopy in the IR and in the visible region. Dissociation of one of the carbonyl groups proved to be faster than the time resolution of the experiment. The present experiments do not allow us to specify whether all excited molecules dissociate or whether internal conversion/intersystem crossing competes with dissociation. The quantum yield studies indicate that only 30% of the molecules will react to form the solvated product Ru(dcbpy)I_2(CO)(EtOH). Part of the dissociated CO groups most probably recombine with the five-coordinated intermediate species due the cage effect provided by the first solvation shell. The results indicate that also recovery of the parent molecules, either via recombination, internal conversion/intersystem crossing or both, occurs on subpicosecond time scales. Our data suggest that the relaxation pathways of the parent molecules go through intermediate electronic states. The observed kinetics in the time window of the present experiments reflect electronic and vibrational relaxation of the recovered parent molecules and solvated product molecules. Cooling of the parent is biexponential with time constants of 4 and 70 ps, whereas the relaxation of product is a slower process occurring in 18 ps and in 270 ps, respectively.

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