

Vibrational relaxation of $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$): Effect of metal mass on vibrational cooling dynamics and non-Boltzmann internal energy distributions

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The vibrational relaxation dynamics following the dissociation of $\text{C}\equiv\text{O}$ from $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) have been studied with picosecond transient absorption spectroscopy. After dissociation of $\text{C}\equiv\text{O}$, the pentacarbonyl species forms a complex with a solvent molecule. The cooling of these solvated pentacarbonyl complexes was monitored from 1 ps to 1 ns and different rates for vibrational relaxation were found for each of these three compounds. The $\text{W}(\text{CO})_5 \cdot \text{S}$ ($\text{S} = \text{cyclohexane}$) vibrationally relaxes in 35 ps, whereas $\text{Mo}(\text{CO})_5 \cdot \text{S}$ relaxes twice as quickly, 18 ps. This result is surprising because the higher density of states in $\text{W}(\text{CO})_5 \cdot \text{S}$ would be expected to lead to faster cooling of the hot solvated complex. The primary cooling of $\text{Cr}(\text{CO})_5 \cdot \text{S}$ is completed in 18 ps just as in $\text{Mo}(\text{CO})_5 \cdot \text{S}$, but a slower cooling of approximately 150 ps is also present. This component is assigned to vibrational relaxation of the $\text{C}\equiv\text{O}$ stretching mode. From comparisons with other studies, it appears that the existence of this slower cooling component is present only in first row transition metal carbonyls.

I. INTRODUCTION

Recently, there has been a great deal of interest in the study of photodissociation, solvation and vibrational relaxation of transition metal carbonyls in solution using ultrafast time-resolved laser techniques.¹⁻⁸ The metal carbonyls are ideally suited for study of these processes for several reasons. First, the metal carbonyls provide a rich diversity of chemical structures and reactions, so that they can serve as model systems for the study of a variety of fundamental processes including isomerization, dissociation, and curve crossing.⁹ Moreover, transition metal carbonyls have strong electronic transitions in the visible and ultraviolet, making them experimentally attractive. In addition, synthetic and spectroscopic studies of transition metal carbonyls have provided extensive information about the bonding and stability of these compounds.⁹ Finally, many studies have been performed on the reaction kinetics of these compounds on the nanosecond and microsecond time scales¹⁰⁻¹² which provide important information for identifying transient species and ultrafast processes.

Some of the most thorough ultrafast work done on metal carbonyls is a series of studies conducted on $\text{Cr}(\text{CO})_6$ using transient visible spectroscopic techniques.^{1,2,3(a)} In these experiments, excitation across a strong, broad absorption band with a maximum near 290 nm, assigned to a $M \rightarrow \pi^* \text{C}\equiv\text{O}$ charge transfer transition, causes efficient ($\phi_{\text{dis}} = 0.7$ in alkane solution) cleavage of the $\text{Cr}-\text{CO}$ bond.¹³ These studies determined that the molecule dissociates in < 500 fs,¹ and that the pentacarbonyl fragment begins to associate with a solvent molecule (S) to

form a vibrationally excited $\text{Cr}(\text{CO})_5 \cdot \text{S}$ complex in about 1.5 ps.^{1,2} The solvated species then cools in cyclohexane in 17 ps.^{3(a)} Finally, long time scale studies have shown the cool, solvated $M(\text{CO})_5 \cdot \text{S}$ complex is stable out to the microsecond regime¹² (and longer depending on the electron donating ability of the solvent).

There is still, however, one important part of the dynamics of $\text{Cr}(\text{CO})_6$ dissociation that remains ambiguous. Some studies have indicated that additional cooling takes place on a time scale longer than 17 ps.⁷ In a recent study using transient Raman spectroscopy, Hopkins and co-workers suggested that cooling in some modes of the solvated complex, including the $\text{C}\equiv\text{O}$ stretch, may take as long as 150 ps.⁷ This is consistent with another study by Heilweil and co-workers who directly excited the $\text{C}\equiv\text{O}$ stretching mode of the ground electronic state $\text{Cr}(\text{CO})_6$ with picosecond infrared pulses and found that cooling from this mode takes place on the 150 ps time scale.^{5(b)} This longer cooling process has not been observed in any visible ultrafast spectroscopic studies done on $\text{Cr}(\text{CO})_5 \cdot \text{S}$. In this paper, we present evidence for the presence of dual cooling rates in the vibrational relaxation of $\text{Cr}(\text{CO})_5 \cdot \text{S}$ through a quantitative examination of the transient electronic absorption spectrum. In addition, we will be addressing the generality of the $\text{Cr}(\text{CO})_6$ results to $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ in this study. A similar study performed by Joly and Nelson found that all three $M(\text{CO})_6$ ($M = \text{Cr}, \text{Mo}, \text{W}$) compounds are dissociated in < 500 fs, that solvent complexation occurs in a 0.5–5 ps interval and that vibrational relaxation happens in the 5–50 ps regime. No qualitative differences in the reaction dynamics of $M(\text{CO})_6$ were found upon changing the identity of M from Cr to Mo to W . Joly and Nelson focused their attention on making a careful comparison of the dissociation process for the three complexes; however, a quantitative comparison

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of the dynamics on longer timescale was not performed.

In this study, we will establish the important parameters involved in the vibrational relaxation dynamics after dissociation by quantitatively comparing the dynamics of $M(\text{CO})_6$ ($M=\text{Cr}, \text{Mo}, \text{W}$) on the 1 ps to 1 ns timescale. We use transient visible spectroscopy to monitor the reaction products after dissociation of a $\text{C}\equiv\text{O}$. While our results are in agreement with those of Joly and Nelson in that there are similarities in the vibrational relaxation dynamics of these species, we have also found important differences in the cooling dynamics of each of the solvated pentacarbonyl complexes especially on the longer timescales.

Section II will discuss the materials, experimental procedure, and apparatus used for these experiments. In Sec. III the results will be presented, and in Sec. IV a discussion on several important differences in the vibrational relaxation of the solvated species will be given. Finally, the results will be summarized in Sec. V.

II. EXPERIMENT

A. Experimental procedures

These experiments were performed using picosecond transient absorption spectroscopy based on a pump-probe system reported earlier.¹⁴ Briefly, a mode-locked argon ion laser synchronously pumps a dye laser to produce 1–2 ps pulses at 590 nm. These pulses are amplified in a three stage dye cell amplifier pumped by the second harmonic of a 10 Hz, Q-switched Nd:YAG laser. The final output consists of pulses ~ 1 ps in duration with an energy of ~ 1 mJ/pulse at 10 Hz. The light is doubled in a 1 mm thick KDP crystal to produce 0.1 mJ, 295 nm pump pulses for photodissociation. The residual fundamental light is focused into a 5 cm cell containing water or acetone to generate a white-light picosecond continuum. Bandpass interference filters, 10 nm full width at half maximum (FWHM), are used to select a portion of the continuum for use as the probe light.

The 295 nm pump light is passed through a variable delay stage before arriving at the sample. The probe light is split into signal and reference beams, collected on large area photodiodes (EG&G DT-110) and processed by a 386 computer-controlled gated integrator (LeCroy CA-MAC 2323 and 2249SG). The typical shot-to-shot spread in the ratios is 0.2% (1 s.d.).

The pump and probe beams are focused collinearly into the sample with a 10 cm focal length lens, giving an estimated spot size of 200 μm at the sample. Typical signal sizes are changes in absorption on the order of 0.2%. The uv pump power intensity is attenuated to 3–8 μJ so that no transient signal is observed from the neat solvent; large uv pump intensities can result in multiphoton ionization of the pure solvents, resulting in large transient absorption signals from the radical cations. The observed signals are found to vary linearly with pump intensity and are independent of probe intensity, indicating that the signals are not due to multiphoton processes.

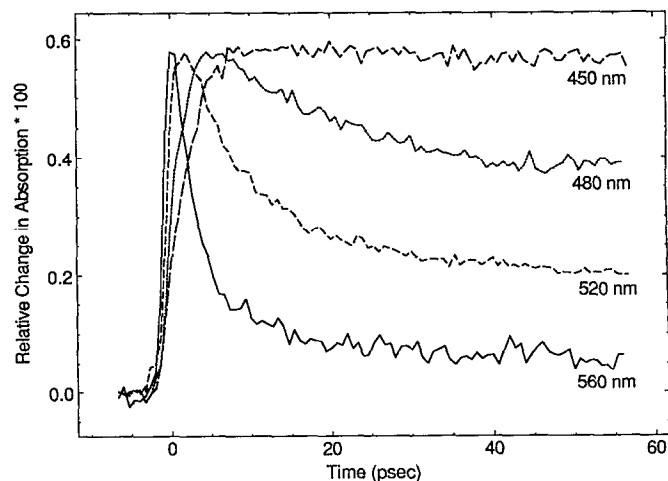


FIG. 1. Transient absorption of $\text{W}(\text{CO})_6$ (5 mM) in cyclohexane pumped with 295 nm light and probed with 560, 520, 480, and 450 nm. The parameters of the best fits to the data are in Table I.

B. Materials

The transition metal carbonyls, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$, were obtained from Pressure Chemical Company and used without further purification. Spectrograde cyclohexane from Aldrich was used as received for all of the solutions. Samples of 3–5 mM $M(\text{CO})_6$ in cyclohexane were flowed through a dye laser nozzle (Spectra-Physics) to produce an optically flat, 100 μm thick sample at the laser focus. A jet was used, instead of a flow cell, to prevent photoproduct from building up on cell walls. The flow rate was more than sufficient to ensure that a fresh sample volume was being probed every laser shot at 10 Hz.

III. RESULTS

Picosecond transient absorption spectroscopy was used to monitor the photodissociation of $\text{C}\equiv\text{O}$ from $M(\text{CO})_6$ ($M=\text{Cr}, \text{Mo}, \text{W}$). The metal carbonyls were excited at 295 nm, near the center of an absorption band assigned to a $M\rightarrow\pi^*$ $\text{C}\equiv\text{O}$ charge transfer transition in $M(\text{CO})_6$.⁹ The absorption of the photoproducts was measured at a variety of wavelengths in the visible region of the spectrum on the timescale of 1 ps to 1 ns. In Figs. 1 and 2 the transient absorption at a variety of probe wavelengths produced over the first 60 ps after excitation of $\text{W}(\text{CO})_6$ is shown. The fitting parameters for all the data are shown in Table I. All data is fit to a convoluted 1 ps Gaussian pulse. The components used to fit the data may include an exponential rise, a single or double exponential decay, and an offset as noted in Table I. The first species observed after photodissociation of $\text{W}(\text{CO})_6$ absorbs at 560 nm. This absorption has a pulse-width limited rise (≤ 1 ps). After the rise the absorption at 560 nm decays in a double exponential manner; the first and larger component decaying in about 3 ps, and the second, minor component decaying in about 29 ps. At 520 nm a similar absorption profile is observed. In this case, however, the initial rise is not quite pulse-width limited (1–2 ps), and the fast decay has

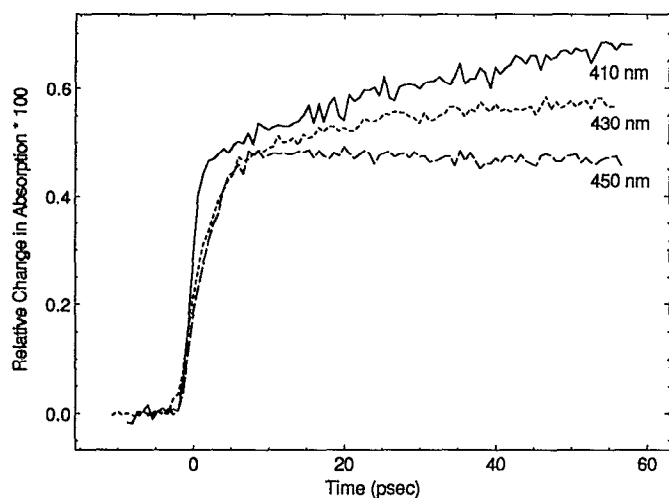


FIG. 2. Transient absorption of $\text{W}(\text{CO})_6$ (5 mM) in cyclohexane pumped with 295 nm light and probed with 450, 430, and 410 nm. The parameters of the best fits to the data are in Table I.

slowed to about 6 ps. No slow component is present, but an offset due to the absorption of the cooled, solvated species is present. These trends continue further to the blue. At 480 nm the rise of the absorption has slowed to 2–3 ps and the decay is about 16 ps. To the blue of 480 nm the profile of the transient absorption changes markedly. At 450 nm the absorption rises in about 3–4 ps and then remains constant. For transient absorptions to the blue of 450 nm the absorption continues to rise throughout the first 60 ps as shown in Fig. 2. At 430 nm there is a fast rise in the absorption of 3 ps and then a slower rise of about 30 ps. At 410 nm the fast rise becomes pulse-width limited and the slow rise is about 42 ps.

As mentioned earlier, there are similarities in the dynamics of all three of these species. For $\text{Cr}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$, Figs. 3 and 4 and Figs. 5 and 6, respectively, the same general trends hold. In all cases there is an initial absorption at redder wavelengths that blue shifts as a function of time. At a particular wavelength the absorption rises quickly and then remains constant. While at bluer wavelengths, the absorption rises throughout the first 60 ps. Although these general trends hold for all three compounds, the actual rates vary by as much as a factor of 2 at analogous wavelengths for the different compounds. Furthermore, there is one component that was found to be qualitatively different for one compound. In the scans at redder wavelengths for $\text{Cr}(\text{CO})_6$ a very slow decay, about 150 ps, was observed, as shown in Fig. 7.

IV. DISCUSSION

The photolysis of $M(\text{CO})_6$ ($M=\text{Cr}, \text{Mo}, \text{W}$) has been studied previously on the picosecond and femtosecond time scales. It was found that dissociation occurs in < 500 fs, complexation of a solvent molecule begins between 0.5 and 5 ps and that vibrational relaxation occurs in the first 50 ps for all three species.¹ Our experimental results are in agreement with those observations. The emphasis of the

TABLE I. Parameters for the best fits to the data for $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, and $\text{W}(\text{CO})_6$ at a variety of probe wavelengths.

Molecule	Wavelength (nm)	Time constants (ps)	Pre-exponential factor ^a
$\text{W}(\text{CO})_6$	410	< 1	-0.24
		42	-0.17
	430	3	-0.84
		30	-0.31
	450	3	-0.49
		480	2
		16	0.26
		offset	0.33
	520	6	0.48
		offset	0.21
	560	3	0.29
		29	0.04
		offset	0.02
$\text{Cr}(\text{CO})_6$	470	< 1	-0.13
		9	0.02
		25	-0.09
	500	< 1	-0.20
		18	-0.17
	530	140	0.03
		offset	0.13
	580	20	0.18
		offset	0.35
	620	12	0.23
		150	0.09
	offset	0.13	
660	8	0.30	
	170	0.11	
	offset	0.06	
$\text{Mo}(\text{CO})_6$	420	< 1	-0.10
		18	-0.25
	440	< 1	-0.04
		10	-0.13
	460	8	-0.15
		35	0.08
		offset	0.15
	480	5	-0.15
		28	0.15
		offset	0.13
	500	22	0.19
offset		0.07	
520	20	0.17	
	540	4	0.09
	18	0.10	
570	3	0.15	
	23	0.04	

^aNegative preexponential factors correspond to an increase in absorption; positive correspond to a decrease in absorption

present study, however, is on comparing the vibrational relaxations of $M(\text{CO})_5 \cdot \text{S}$ to determine the effect of different metal atoms. To compare the data for the vibrational relaxation of these three compounds, it is first necessary to identify the trends in the transient absorptions that correspond to vibrational relaxation. From matrix^{10,11} and longer time scale^{9,12} studies, it has been determined that the cooled, solvated, pentacarbonyl species has an absorption centered in the visible region of the spectrum which is not present for the parent hexacarbonyl species. The λ_{max}

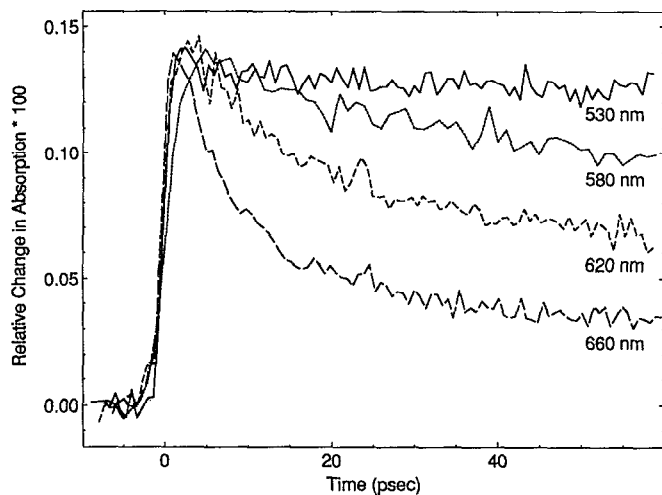


FIG. 3. Transient absorption of $\text{Cr}(\text{CO})_6$ (5 mM) in cyclohexane pumped with 295 nm light and probed with 660, 620, 580, and 530 nm. The parameters of the best fits to the data are in Table I.

for these species is dependent upon the solvating species (the more electron donating ability the bluer the absorption) and the identity of the metal center

$$\lambda_{\text{max}}[\text{W}(\text{CO})_5 \cdot \text{S}] \approx \lambda_{\text{max}}[\text{Mo}(\text{CO})_5 \cdot \text{S}] < \lambda_{\text{max}}[\text{Cr}(\text{CO})_5 \cdot \text{S}].$$

For the cyclohexane solvated species, the absorption peaks are $\lambda_{\text{max}}[\text{W}(\text{CO})_5 \cdot \text{S}] = 415$ nm, $\lambda_{\text{max}}[\text{Mo}(\text{CO})_5 \cdot \text{S}] = 415$ nm, and $\lambda_{\text{max}}[\text{Cr}(\text{CO})_5 \cdot \text{S}] = 500$ nm.¹⁵ To accurately compare the relaxation dynamics of these three species, it is necessary to compare wavelengths relative to the absorption maximum of the cool, solvated species. In previous studies, a common transient spectroscopic signature has been identified for the process of vibrational relaxation. It has been found^{14,16} that a vibrationally excited species,

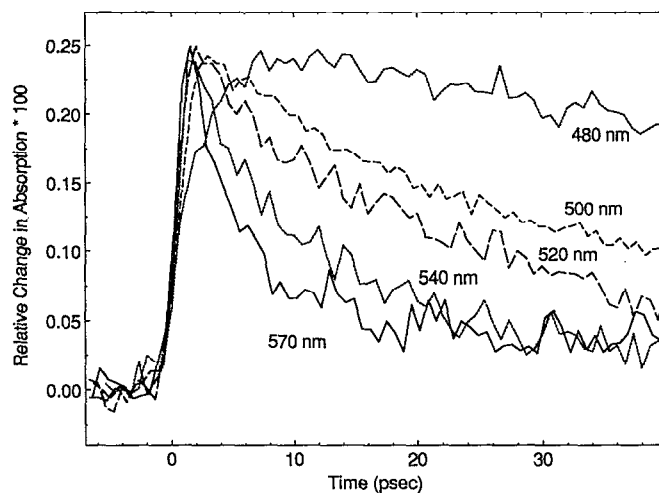


FIG. 5. Transient absorption of $\text{Mo}(\text{CO})_6$ (5 mM) in cyclohexane pumped with 295 nm light and probed with 570, 540, 520, 500, and 480 nm. The parameters of the best fits to the data are in Table I.

in this case the solvating pentacarbonyl species, often absorbs to the red of its cool λ_{max} because the species is high in the potential energy well, and therefore closer to the excited electronic state. For $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$, the absorption of the highly vibrationally excited species is centered at 560 nm. As the species starts to cool and relax down the well, the absorption at these reddest wavelengths disappears quickly while the absorption of cooler species, more to the blue, increases [520 nm and 480 nm for $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$]. As the species cools, the rate of cooling slows down. This slowing is due to two factors. First, as the internal temperature of the solvating pentacarbonyl decreases, the difference in temperature between the metal carbonyl and the solvent becomes smaller and the rate of cooling slows. In addition, the anharmonicity of the potential will assist cooling near the top of the well. At

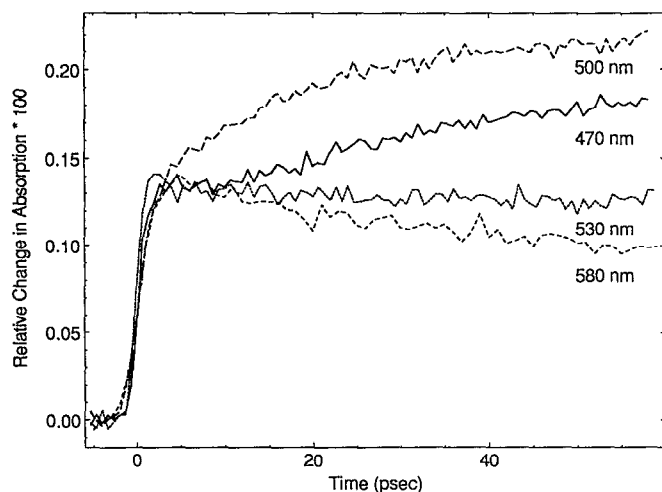


FIG. 4. Transient absorption of $\text{Cr}(\text{CO})_6$ (5 mM) in cyclohexane pumped with 295 nm light and probed with 580, 530, 500, and 470 nm. The parameters of the best fits to the data are in Table I.

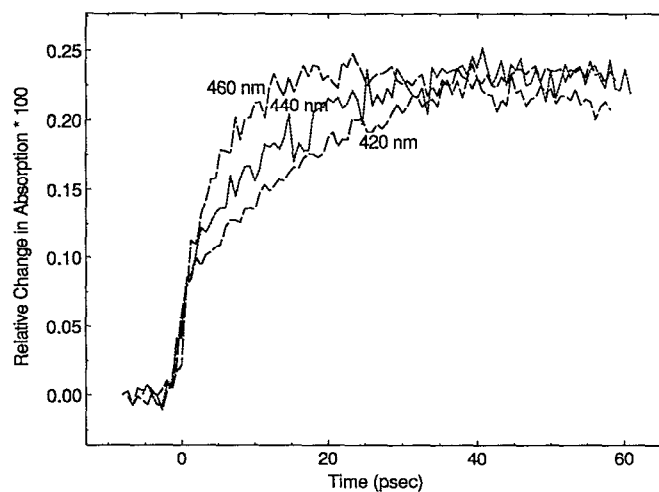


FIG. 6. Transient absorption of $\text{Mo}(\text{CO})_6$ (5 mM) in cyclohexane pumped with 295 nm light and probed with 460, 440, and 420 nm. The parameters of the best fits to the data are in Table I.

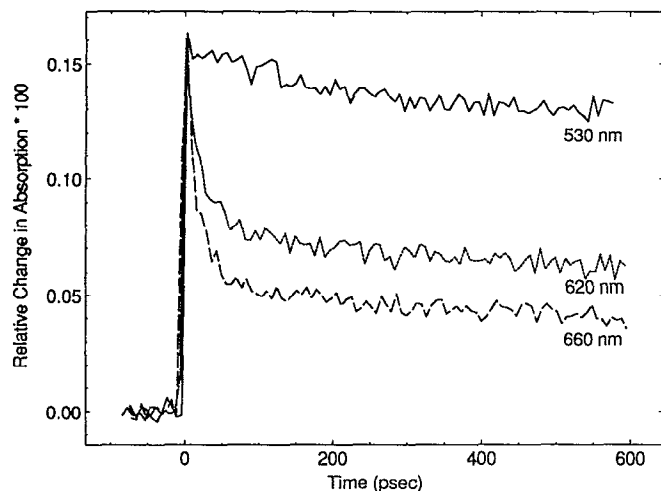


FIG. 7. Transient absorption of $\text{Cr}(\text{CO})_6$ (5 mM) in cyclohexane pumped with 295 nm light and probed with 660, 620, and 530 nm on a longer time scale than in Figs. 1–6. At each of these wavelengths, a 150 ps component is present. The parameters of the best fits to the data are in Table I.

the top of the well the spacing between the energy levels is smaller. This allows better coupling between the vibrational modes of the metal carbonyl and the low energy rotational and translational modes of the solvent which have been shown to be important modes for accepting energy in vibrational relaxation.¹⁴ This slowing can be seen in $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$ at 520 and 480 nm. In both cases the cooler species (absorbing at 520 and 480 nm) do not appear as fast as the hotter species (absorbing at 560 nm), and the disappearance of these cooler species is slower. At bluer wavelengths, there may be a region where the changes in population due to vibrational relaxation and the changes in absorption of the different species roughly balance each other and after the initial rise at these wavelengths the absorption remains essentially constant. This corresponds to 450 nm for $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$. Finally, as the species relaxes to the bottom of the potential well and comes into equilibrium with the solvent, its absorption increases at wavelengths that have been found to be the λ_{max} for the cool, solvated species. For $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$ this corresponds to the absorption near 415 nm. All three compounds show this trend in their transient absorption spectrum, and in each case it is assigned to vibrational relaxation.

Although these similarities exist, important differences between the dynamics of the vibrational relaxation of these complexes are also observed. One difference is a very long (> 100 ps) component in the decay of vibrationally excited $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$. Figure 7 shows the transient absorption of this complex at 530, 620, and 660 nm. At all three wavelengths the long component was measured to be about 150 ps. The relaxations of the tungsten and molybdenum complexes show no corresponding long component in those systems. This long component was first observed in our group in the initial studies of $\text{Cr}(\text{CO})_6$,¹⁷ but was not assigned until subsequent vibrational work was

completed. Hopkins and co-workers used transient Raman spectroscopy to study the vibrational relaxation of $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$ and found a relaxation time similar to this long component for the vibrationally excited $\text{C}\equiv\text{O}$ stretch in $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$.⁷ This is also the time scale for relaxation of vibrationally excited $\text{C}\equiv\text{O}$ on $\text{Cr}(\text{CO})_6$ measured by Heilweil and co-workers.^{5b} Based on the similarity in time scale with these studies, we assign this long component in the transient absorption of $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$ to relaxation of the vibrationally excited $\text{C}\equiv\text{O}$ stretch.

When probed to the blue of 620 nm, closer to the absorption maximum of the cooled product (500 nm), the long component is absent over the region 570–610 nm, but reappears again near 530 nm. There are two possible explanations for the reappearance of the long component at 530 nm. First, the absorption spectrum of the species with a $\text{C}\equiv\text{O}$ vibrationally excited is not known. It could be that this species has a larger absorption cross section at 530 nm than the completely cooled complex. If this is the case then we are just monitoring the disappearance of the same species at three different wavelengths (530, 620, and 660 nm). Another possibility is that increased absorption at 530 nm could be due to population in low energy modes of the $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$. The similarity of the time scales for these two features could then be interpreted as vibrational energy from the high frequency modes (absorbing at 620 nm) being transferred to lower frequency modes (absorbing at 530 nm) which then transfer the energy to the solvent. If the energy transfer to the solvent (intermolecular) was faster than high frequency to low frequency energy transfer (intramolecular), then a small component with the same decay rate as the high frequency to low frequency transfer rate should be seen when probing the low frequency modes at 530 nm. The long component is not seen at intermediate wavelengths (570–610 nm) because the $\sim 2000 \text{ cm}^{-1}$ of energy that is transferred from the high frequency $\text{C}\equiv\text{O}$ stretch mode to the low frequency modes is quickly distributed over the entire complex via efficient intramolecular vibrational energy redistribution so that the internal temperature of the complex is never high enough to absorb above 530 nm. This scheme is also in agreement with the previously mentioned transient Raman work.⁷ In that study, it was found that the $\text{M}-\text{CO}$ bond relaxed with the same rate as the high frequency $\text{C}\equiv\text{O}$ stretch mode, with a time constant of approximately 150 ps.

In an earlier study of a similar molecule, $\text{Mn}_2(\text{CO})_{10}$, it was found that the relaxation of $\text{Mn}_2(\text{CO})_9$ also had a component > 100 ps.^{3(b)} It was also attributed to vibrational relaxation through the $\text{C}\equiv\text{O}$ stretch mode. Other work completed in this laboratory on the third row transition metal complexes has shown that there is no long component in the relaxation dynamics of $\text{Re}_2(\text{CO})_9$. As discussed earlier, we have found no long component in the relaxation of either the molybdenum or the tungsten carbonyl complexes. Therefore, of the five compounds mentioned, $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$, $\text{W}(\text{CO})_6$, $\text{Re}_2(\text{CO})_{10}$, and $\text{Mn}_2(\text{CO})_{10}$, the only two which show anomalously long

relaxation times are the ones with first row transition metals, $\text{Cr}(\text{CO})_6$ and $\text{Mn}_2(\text{CO})_{10}$. There are several possible explanations why these lighter transition metal carbonyls might show the long component in their dynamics. First, the $\text{C}\equiv\text{O}$ stretch may not be significantly excited in the dissociation of the heavier metal carbonyls. The additional metal mass could affect the partitioning of the available energy from photodissociation among the different degrees of freedom. The heavier mass would lead to less coupling between the $\text{C}\equiv\text{O}$ stretch mode in $M(\text{CO})_5$ and the $M\text{--CO}$ dissociation coordinate and thus less $\text{C}\equiv\text{O}$ stretch excitation. Another possible explanation for the absence of a slow component in the heavier transition metal carbonyls is that the energy deposited in the $\text{C}\equiv\text{O}$ stretch of these species is transferred more quickly to other modes of the molecule or solvent. However, it was found by Heilweil and coworkers that energy generally took *longer* to transfer from the $\text{C}\equiv\text{O}$ stretch to the low energy modes in $\text{W}(\text{CO})_6$ than in $\text{Cr}(\text{CO})_6$.^{5(b)} Based on this finding, it is likely that the amount of energy initially deposited in the $\text{C}\equiv\text{O}$ stretch is the most important factor, and the stronger coupling of the $\text{C}\equiv\text{O}$ stretch mode to the dissociation coordinate in $\text{Cr}(\text{CO})_6$ causes this larger deposit of energy.

Another important difference in the dynamics of these compounds is the amount of time needed to reach thermal equilibrium with the solvent. The absorption of these solvated pentacarbonyl species near their maximum is plotted in Figs. 2, 4, and 6. All three show a fast rise, which is attributed to the initial formation of a bond with a solvent molecule, followed by a slow rise which is assigned to relaxation of the vibrationally excited species. For both $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$ and $\text{Mo}(\text{CO})_5 \cdot \text{cyclohexane}$ the initial fast rise is pulse-width limited, and the slow rise is approximately 18 ps. For the tungsten complex, however, the fast rise is not pulse-width limited, 3 ps, and the slower rise is approximately 35 ps. Both of these slower rises in the tungsten data point to slower vibrational relaxation in the tungsten complex than either the molybdenum or chromium complexes. The slower fast component implies that it takes longer for the naked pentacarbonyl species to lose enough energy to begin to form a bond with a solvent molecule, and the slower long rise implies that it takes longer for the solvated species to relax to thermal equilibrium with the solvent. This is a surprising result because one might expect a species with a higher density of states such as $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$ to have modes which match those of the solvent better and therefore, have a faster cooling rate. A similar effect has been noted for the vibrational relaxation of asymmetric mixed-valent transition metal dimers.¹⁸ In these studies, it was noted that energy transfer rates are significantly decreased upon substituting osmium for ruthenium. The reason for the slower cooling in the heavier metal systems is not apparent at this time. Perhaps the lighter species have resonances that fortuitously match the resonances in the solvent better or the internal modes of the lighter species are better coupled to allow a more even and faster cooling. These questions are currently being addressed in our lab.

Regardless of the causes, both the 150 ps component in

the vibrational relaxation of $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$ and the longer primary cooling of $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$ show that some simple ideas about energy distribution and dissipation do not apply even in these moderately sized molecules. For example, the concept of internal temperature is often used when considering the intramolecular vibrational energy redistribution after absorption of a photon. However, in cases such as $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$ where different modes of the molecule are only weakly coupled, a single internal temperature, calculated as a Boltzmann distribution of the available energy over all the modes of the molecule,¹⁹ is clearly insufficient. Instead, a non-Boltzmann type of description of the individual modes is necessary to accurately describe the internal energy distribution in these systems.

V. CONCLUSION

We have studied the photodissociation dynamics of $\text{Cr}(\text{CO})_6$, $\text{Mo}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ and determined the vibrational relaxation rates of their photoproducts in cyclohexane. All the molecules dissociate in <1 ps. $\text{Cr}(\text{CO})_5$ and $\text{Mo}(\text{CO})_5$ are found to associate with a solvent in <1 ps. $\text{W}(\text{CO})_5$ takes ~ 3 ps to associate with a solvent molecule. The cooling of the solvated species, $\text{Cr}(\text{CO})_5 \cdot \text{S}$ and $\text{Mo}(\text{CO})_5 \cdot \text{S}$ ($\text{S} = \text{cyclohexane}$), occurs with a time constant of 18 ps, while $\text{W}(\text{CO})_5 \cdot \text{S}$ takes twice as long, 35 ps. A slow decay component observed in $\text{Cr}(\text{CO})_5 \cdot \text{cyclohexane}$ is assigned to relaxation of the high frequency $\text{C}\equiv\text{O}$ stretch to low frequency modes in the molecule. This slow component is not present in the heavier transition metal carbonyls, $\text{Mo}(\text{CO})_5 \cdot \text{cyclohexane}$ and $\text{W}(\text{CO})_5 \cdot \text{cyclohexane}$. This anomalously long component is also reported in the relaxation of $\text{Mn}_2(\text{CO})_9$, another first row metal carbonyl, but not in $\text{Re}_2(\text{CO})_{10}$, a second row metal carbonyl. One possible explanation for the trend of first row transition metal/long vibrational relaxation is that the $\text{C}\equiv\text{O}$ stretch mode in $M(\text{CO})_5$ is more likely to be excited during the dissociation in the lighter first row transition metals. A $\text{C}\equiv\text{O}$ stretch mode is more likely to be excited in the lighter $\text{Cr}(\text{CO})_5$ fragment because its lighter mass increases the amount of kinetic energy deposited in the fragment. This higher kinetic energy increases the probability of energy being transferred into the high frequency $\text{C}\equiv\text{O}$ stretch. More generally these results begin to address the important issue of the effect of the internal structure on the reaction dynamics of moderately sized molecules. This is a fundamental issue that must be addressed to advance our understanding from the dynamics of diatomics to the more chemically relevant moderate and large sized molecules. These results have important implications in understanding the role of internal structure in the energy relaxation dynamics of moderately sized molecules in solution.

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